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USSR Report

CHEMISTRY

No. 87



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ALKALOIDS

UDC 615.322 : 582.951.4 : 547.944.3].012.8

ALKALOID EXTRACTION FROM SCOPOLIA GRASS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 3, Mar 82
(manuscript received 8 Jan 81) pp 338-341

MININA, S. A., GROMOVA, N. A., FILIPIN, N. A., KOMOVSKIY, B. K.,
GVIRTS, M. V. and LOKSIN, B. A., Leningrad Chemical Pharmaceutical
Institute; "Progress" Scientific Production Association, Leningrad

[Abstract] Continuing earlier research (reported in this journal, No 11, Nov 74, pp 56-60 and No 3, Mar 74, pp 135-137), the effectiveness of extraction equipment is summarized. The process begins with evacuation of air from the extraction chamber and hence from the plant material in the chamber by steam pressure, followed by injecting an extractant with rapid condensation, during which the extractant enters the plant cells. Repeated forced removal of extract from the plant material and refilling with extractant leads to convective diffusion during which medicinal substances are removed along with the extractant. Water soluble alkaloid salts were obtained in this manner with 98% yield in 30 minutes with the second, refined extraction system summarized, involving alternating vacuum and heating steps with evacuation stages. The results obtained with the latter system were used in further research seeking to obtain a more concentrated extract. Figures 2; references 6 (Russian).
[180-12131]

ANALYTICAL CHEMISTRY

UDC 541.127:546.18

REACTIONS LEADING TO FORMATION OF ATOMIC PHOSPHORUS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 1, Jan 82 (manuscript received 25 Nov 80) pp 22-25

ALEKSANDROV, Ye. N., ARUTYUNOV, V. S., DUBROVINA, I. V. and KOZLOV, S. N.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] The rate constants of phosphorus atom formation were studied in $H + PCl_3$ and $H + P_4$ reactions. Variation of the rate of heterogeneous decay of atoms was checked upon addition of small quantities of P_4 or PCl_3 to the flow. The rate constants of the heterogeneous decay of atoms were determined by variation of the flow velocity or introduction of a quartz rod described previously. The resonance fluorescent method was used under flow conditions in the temperature range of 300-670K to determine the rate constants. Atomic phosphorus was recorded in the products of the reactions in concentrations comparable to concentrations of the expended hydrogen atoms. Figures 2; references 9: 6 Russian, 3 Western.

[128-6521]

UDC 546.814

TIN HYDROXOORTHOPHOSPHATE AND HYDROXOORTHOARSENATE

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 2, Feb 82
(manuscript received 2 Mar 81) pp 339-343

CHERNORUKOV, N. G., SIBRINA, G. F. and YEGOROV, N. P., Gor'kiy State
University imeni N. I. Lobachevskiy

[Abstract] Study of new compounds $Sn(OH)PO_4$ and $Sn(OH)AsO_4$ was conducted by infrared spectroscopic and roentgenographic and thermographic methods to establish their functional composition, structure and structural similarity. The compounds revealed an isostructure between them and are similar in structure to the known compound $Ge(OA)PO_4$. The crystallographic and infrared

spectroscopic characteristics of the compounds and the products of their thermal breakdown were determined in the temperature range of 20-1000°C. The behavior of $\text{Sn}(\text{OH})\text{PO}_4$ and $\text{Sn}(\text{OH})\text{AsO}_4$ upon heating confirms their functional composition and structure. Hydroxyortho-derivative compositions of $\text{Sn}(\text{OH})\text{XO}_4$ in which SnO_6 octahedrons are linked in the chain along one of the fourth order axes and are combined into a crystal lattice by phosphate or arsenate tetrahedrons, exist in a number of tin hydroxoorthophosphates and hydroxoorthoarsenates. Figures 3; references 11: 4 Russian, 7 Western. [132-6521]

UDC 541.49+546.972

INVESTIGATION OF CRYSTALLINE STRUCTURE OF $[\text{Rh}_2(\text{H}_2\text{PO}_4)_4(\text{H}_2\text{O})_2]$

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 2, Feb 82
(manuscript received 30 Apr 81) pp 417-423

DIKAREVA, L. M., SADIKOV, G. G., PORAY-KOSHITS, M. A., BARANOVSKIY, I. b., ABDULLAYEV, S. S. and SHCHELOKOV, R. N., Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR Academy of Sciences

[Abstract] X-ray diffraction study of $[\text{Rh}_2(\text{H}_2\text{PO}_4)_4(\text{H}_2\text{O})_2]$ crystals showed that the complex has dimer structure with four bridge H_2PO_4 -groups. The distance of Rh-Rh is equal to 2.487 (1) angstroms. The water molecules are in the axial position in trans-position to the Rh-Rh bond; $\text{Rh} - \text{O}_{\text{H}_2\text{O}} = 2.29$

angstroms and $\text{Rh} - \text{O}_{\text{phos}} = 2.04$ angstroms.
[132-6521]

UDC 546.23 + 536.77

FREE ENERGY OF POLYSELENIDE ANION FORMATION IN AQUEOUS SOLUTIONS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 2, Feb 82
(manuscript received 3 Mar 80) pp 431-433

GLADYSHEV, V. P. and DUBININA, L. K., Institute of Steel and Alloys, Moscow; Kazakh State University imeni S. M. Kirov, Alma-Ata

[Abstract] Free energies of polyselenide ions were calculated for various compositions based on literature data of thermodynamic characteristics of hexagonal selenium and its compounds. The most thermodynamically stable compound under normal conditions is the chain molecule Se_n and not atomic selenium. Based on the equation $\Delta G_{298}^0 = \Delta H_{298}^0 - \Delta TS_{298}^0$ and taking the ΔH_{298}^0 and ΔS_{298}^0 values for atomic selenium to be 0 and 42.5 J/mole respectively, the free energy of atomic selenium formation $\Delta G_{298}^0 \text{Se}$ was calculated to be 12.66 kJ/mole. Based on this result, the ΔG_{298}^0 values for Se_2^{2-} , Se_3^{2-} , Se_4^{2-} and Se_6^{2-} were calculated. These calculated values agreed well with data from electrochemical experiments. References 12: 11 Russian (1 by Western author), 1 Western.
[162-7813]

OXIDATION AND GRAPHITIZATION OF DIAMOND AT LOW PRESSURE

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 2, Feb 82

(manuscript received 7 May 81) pp 495-496

USPENSKAYA, K. S., TOLMACHEV, Yu. N. and FEDOSEYEV, D. V., Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] Oxidation of synthetic diamond powders of varying granularity was studied at different pressures and temperatures (7-400 Pa and 600-1000°C). It was shown that fine powders exhibited surface graphitization along with oxidation at temperatures of 850°C. Coarser particles showed this phenomenon at a higher temperature, namely at 950°C and higher. The thickness of this carbonized layer increased rapidly with elevation of the oxidation temperature and was linearly related to the oxidation time. Figures 1; references 8: 5 Russian, 3 Western (1 by Russian authors). [162-7813]

STRUCTURE AND CHEMICAL SHIFTS OF $\delta^{31}\text{P}$ PHOSPHAZOALKANES

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 18, No 1, Jan-Feb 82 (manuscript received 18 Sep 81) pp 58-65

YEGOROV, Yu. P., KUDRYAVTSEV, A. A., PINCHUK, A. M., MARCHENKO, A. P. and KOVENYA, V. A., Institute of Organic Chemistry, UkSSR Academy of Sciences, Kiev

[Abstract] The values of chemical shifts of ^{31}P nuclei (δ_{P}) represent very informative characteristics of the structure of phosphorus-containing molecules. An attempt was made to develop a general empirical formula relating δ_{P} to structural characteristics of the phosphorus atom substituents. Phosphazoalkanes of the general formula $\text{R}_3\text{P} = \text{NY}$ were investigated, where $\text{R} = (\text{Me}_2\text{N})_3$; $(\text{Et}_2\text{N})_3$, $(\text{Et}_2\text{N})_2\text{CCl}_3$, $(\text{Et}_2\text{N})_2\text{CCl}_2$, $(\text{CCl}_3)_2\text{CCl}$ and $(\text{CCl}_3)_3$ and $\text{Y} = \text{H}$, Me, Et, Pro, But, Hept, 1-Pro and cyc-Hex. Progression in the direction listed of either of the substituents (while keeping the other constant) led to a shift of δ_{P} towards higher fields. A function was developed and constants were calculated relating these parameters. Finally, a formula was developed for the calculation of δ_{P} for $\text{R}_3\text{P} = \text{NY}$ compounds. The calculated values agreed reasonably well with experimentally determined ones. Figures 2; references 23: 12 Russian, 11 Western. [164-7813]

NMR STUDY OF STRUCTURE AND STABILITY OF DIBENZOMETHYLPHOSPHONYL-20-CORONA-7 COMPLEXES WITH ALKALI AND ALKALINE EARTH METAL IONS

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 18, No 1, Jan-Feb 82 (manuscript received 3 Mar 81) pp 65-71

BIDZILYA, V. A., GOLOVKOVA, L. P., YATSIMIRSKIY, K. B., KESSENIKH, A. V., RYABOKOBYLKO, Yu. S. and SHMELEV, L. V., Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev

[Abstract] The goal of this study was to investigate the effect of solvent polarity on the ability of heterofunctional macrocyclic polyesters MRS (dibenzomethylphosphonyl-20-corona-7) to form complexes with alkali and alkaline earth metal ions. This study was carried out by the NMR method in d_6 -acetone, in which the perchlorates of these metals are completely dissociated. Addition of Li, Ca, Mg, Sr and Ba perchlorates to MRS solution resulted in shifts of all corona proton signals. Na^+ ions showed a different shift sequence, leading the authors to conclude that Na^+ formed a different complex than the other ions. The authors stated that Mg^{2+} and Ca^{2+} formed ML_2^{2+} type complexes, while Li^+ , Na^+ , Sr^{2+} and Ba^{2+} could form either ML_2^{2+} or ML_2^{2+} type complexes. Stability constants were calculated for Li^+ , Na^+ and Ba^{2+} complexes with MRS. Figures 4; references 7: 4 Russian, 3 Western. [164-7813]

UDC 66.547

NITROGEN OXIDE OUTPUT IN THERMOOXIDATIVE NEUTRALIZATION OF AMMONIA GAS

Kiev KHIMICHESKAYA TEKHOLOGIYA in Russian No 2, Mar-Apr 82 pp 48-50

KOLIYENKO, A. G. and KARNAUKH, N. G.

[Abstract] Burning of effluent ammonia and other nitrogen-containing gases by thermooxidative neutralization leads to formation of increased amounts of nitrogen oxides in the atmosphere. Studies are reported here on methods of reducing the nitrogen oxide output at industrial facilities where effluent gases contain ammonia. Methods of reduction include recirculation of cooled combustion products, two-stage and tangential vortex burning and reduced air heating, but these are insufficient due to increased demands for elimination of noxious odors from toxic gases, increased complexity of installations, and required savings for neutralization of ammonia gas. Tests have shown that ammonia gas is the most difficult of several waste gases to burn off due to the minimum 800° C temperature required. The method proposed increases the amount of oxygen-containing waste gases in the furnaces of drying and

heat-generating installations. With delivery of excess amounts of oxygen, the temperature needed for complete neutralization of ammonia gas can be reduced and the costs of cutting nitrogen oxide output minimized. Figures 2. [183-12131]

UDC 632.901 : 634.1/7 : 635.1

CHROMATOGRAPHIC DETERMINATION OF RESIDUAL AMOUNTS OF ORGANOPHOSPHOROUS PESTICIDES IN DRIED FRUITS AND VEGETABLES

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 37, No 3, Mar 82
(manuscript received 3 Apr 80) pp 494-498

ZALUTSKAYA, O. I. and SALASHINSKIY, N. A., Trade and Economics Institute, L'vov

[Abstract] Thin layer chromatography of sorbents was used to determine residues of metaphos, phosphamide and chlorophos found jointly in dried potatoes, carrots, parsley, apples, pears and prunes. Samples of the indicated dried products were ground up and 10 mcg of the pesticides were mixed with 25 g of each as a control. Then test models were prepared of 150 g samples to which maximum permissible amounts of each pesticide were added, with n-hexane to insure equal distribution. After 5-7 days storage, 25 g samples were taken and compared to the control samples. Various extractants were used to separate the pesticides from the dried products. The most effective extraction was achieved by using a 30% solution of acetone in n-hexane, followed by purging of the extracts, separation, and qualitative and quantitative assay using thin layer chromatography. The minimum limits for identifying pesticide content were 1-5 micrograms. References 9: 5 Russian, 4 Western.
[185-12131]

UDC 661.886

OBTAINING WHITE ARSENIC BY OXIDIZING ARSENIC TRISULFIDE

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 81
pp 117-121

RZAYEV, B. Z. and SAYADOV, R. K., Nakhichevan Scientific Center, AzSSR Academy of Sciences

[Abstract] In order to obtain pure white arsenic after original production from arsenic-sulfur ores, the authors used a sulfide method to refine arsenic trisulfide obtained from the Darydag hot springs. 99.5%-Pure As_2S_3 was subjected to volatilization in oxygen in a reactor containing successive

platelike baffles. It was found that as temperatures surpassed 400° C, the degree of oxidation increased, reaching 99.57% between 500 and 600° C. Further temperature increases led to volatilization of arsenic trisulfide and a drop in its oxidation. Increased oxygen feed also reduced oxidation, so that constant delivery of oxygen totaling 2.25 liters brought complete oxidation at a rate of 1 ml/sec. In air the oxidation temperature for maximum results was set at 550° C at 4 ml/sec, using a total of 9.2 liters, and with an air/oxygen mix, the same temperature and an injection rate of 5.4 liters was regarded as optimal. No qualitative variations were noted with different types of oxidants. Figures 3; references 3 (Russian).
[186-12131]

BIOCHEMISTRY

UDC 615.357.453.012.6.002.62 : 547.92

PRODUCTS OF MICROBIOLOGICAL TRANSFORMATION OF 19-HYDROXYSITOSTEROL

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 3, Mar 82
(manuscript received 10 Jun 81) pp 334-338

KOLYVANOVA, T. S., JAYUNOVA, V. I., GABINSKAYA, K. N., KOROBOVA, Yu. N.
and GRINENKO, G. S., All Union Scientific Research Chemical Pharmaceutical
Institute imeni S. Ordzhonikidze, Moscow

[Abstract] Seeking low-cost and readily available raw materials for synthesizing steroid hormones, the authors studied sitosterol (from wood-processing wastes) to determine features of its transformation into 3-acetate of 19-hydroxysitosterol, and of the further product estrone. To select the best conditions for growing necessary bacteria, a culture *Protoaminobacter alboflavum* was chosen, on which the maximum quantity of estrone was formed in 144 hours, with 55% yield from the initial 19-acetate at a temperature of 32° C. This yield was achieved by protection of the steroid skeleton from total destruction by the enzyme disintegration process. Details of synthesis of initial compounds and of culturing are presented in the experimental section. References 6: 2 Russian, 4 Western.
[180-12131]

CATALYSIS

UDC 547.21:542.97:66.094.222

FORMATION, PHASE COMPOSITION, TEXTURE AND CATALYTIC PROPERTIES OF
Co-MgO-CALCIUM-ALUMINA CATALYSTS IN SYNTHESIS OF HYDROCARBONS FROM CO
AND H₂

Moscow NEFTEKHIMIYA in Russian Vol 21, No 6, Nov-Dec 81
(manuscript received 22 Dec 80) pp 863-871

LAPIDUS, A. L., BRUK, I. A., MAL'TSEV, V. V., KHOANG CHONG IEM,
YAKERSON, V. I., GOLOSMAN, Ye. Z., MAMAYEVA, I. A., KALACHEVA, N. B.,
DANYUSHEVSKIY, V. Ya. and NISSENBAUM, V. D., Institute of Organic Chemistry
imeni N. D. Zelinskiy, USSR Academy of Sciences; Novomoskovsk Branch,
State Scientific Research and Planning Institute of the Nitrogen Industry
and Products of Organic Synthesis

[Abstract] The formation of cobalt and calcium-aluminum systems was studied and detailed investigation of them during synthesis of hydrocarbons from carbon monoxide and hydrogen was carried out. The formation of catalysts in which the components of calcium aluminates and basic cobalt and magnesium carbonates interact was studied. The carrier with developed surface and the active component on this surface are created during the reaction. The catalysts show maximum selectivity with respect to synthesis of liquid hydrocarbons from carbon monoxide and hydrogen with 65-84 percent restoration of the metal and dispersion by carbon monoxide chemisorption equal to $6 \cdot 10^{-3}$ to $10 \cdot 10^{-2}$. The yield of liquid hydrocarbons is maximum in the presence of 33Co-3MgO-64talyum treated with hydrogen at 550°C. Cobalt-magnesium oxide-calcium aluminate catalysts are active in synthesis of liquid hydrocarbons. References 17: 15 Russian, 1 Polish, 1 Western. [95-6521]

EFFECT OF AMMONIA ON CATALYTIC PROPERTIES OF ZEOLITE-CONTAINING CATALYST ASHNTs-3 IN ALKYLATION OF PHENOLS BY STYRENE

Moscow NEFTEKHIMIYA in Russian Vol 21, No 6, Nov-Dec 81
(manuscript received 2 Apr 81) pp 885-889

KOLESNICHENKO, N. V., KURASHEV, M. V., ROMANOVSKIY, B. V. and
MENYAYLOV, A. A., Institute of Petrochemical Synthesis imeni A. V. Topchiyev,
USSR Academy of Sciences; Moscow State University imeni M. V. Lomonosov

[Abstract] The effect of preliminary treatment with a mixture of ammonia and a small quantity of water vapor on the catalytic properties of the zeolite-containing catalyst ASHNTs-3 was investigated. Preliminary treatment of the catalyst with an ammonia-water vapor mixture at 250°C for 2 hours results in a considerable increase in the yield of methylbenzylphenols and specifically of 2-(α -methylbenzyl)phenol. Treatment of zeolites with ammonia results in dealuminization of the zeolite body and the appearance of exchange aluminum on the catalyst surface after treatment with ammonia affects the selectivity of the catalyst with respect to formation of 2-(α -methylbenzyl)phenol. The highest yield of methylbenzyl phenols is achieved at 250°C with no less than 4:1 molar ratio of phenol:styrene and at a volumetric rate of 5.5 hr⁻¹. Figures 1; references 9 (Russian).
[95-6521]

KINETICS AND MECHANISM OF CATALYTIC DEGRADATION OF CUMYL HYDROPEROXIDE UNDER ACTION OF SUBSTITUTED 5-TERT-BUTYL-2-HYDROXYPHENYLSULFIDES

Moscow NEFTEKHIMIYA in Russian Vol 21, No 6, Nov-Dec 81
(manuscript received 21 Jan 80) pp 898-905

KULIYEV, F. A., FARZALIYEV, V. M., DENISOV, Ye. T. and VORONKOV, M. G.,
Institute of the Chemistry of Additives, Azerbaijan SSR Academy of Sciences

[Abstract] Catalytic decomposition of cumyl hydroperoxide exposed to substituted hydroxyarylsulfides was investigated in the temperature range of 70-110°C. All eight substituted 2-hydroxyarylsulfides catalytically break down cumyl hydroperoxide. One molecule of the sulfide can break down several hundred to several thousand hydroperoxide molecules depending on the structure. The rate of catalytic decomposition of cumyl hydroperoxide is directly proportional to the inhibitor concentration and to the square of hydroperoxide concentration. The interaction products of methyl-(5-tert-butyl-2-hydroxyphenyl) sulfide with cumyl hydroperoxide are capable of breaking the chain of cumol oxidation repeatedly, up to 10-15 times. Figures 3; references 13: 9 Russian, 4 Western.
[95-6521]

CHEMICAL INDUSTRY

MANAGEMENT BLAMED FOR TURKMEN CHEMICAL PLANT CONSTRUCTION DELAYS

Ashkhabad TURKMENSKAYA ISKRA in Russian 24 Mar 82 p 2

[Article by V. Kazantsev, Communist Party Central Committee instructor, Turkmenistan: "The Price of Overall Supervision"]

[Text] Chemists and petroleum refiners have much to do in the 11th Five-Year Plan. A significant increase in output of mineral fertilizers, chemical raw material and different petroleum products is contemplated because of the development of operational capacities and the putting into service of new capacities. It is a matter of honor for labor collectives and party organizations to complete the renovation and construction of projects on schedule.

We are talking about the TZAU [Turkmen Nitrogen Fertilizer Plant], the Chardzhou Petroleum Refining Complex, PVS-350 [ground-air liaison post] of the Gaurdak sulfur plant and the moderated coking installation of the Krasnovodsk Petroleum Refining Enterprise. They now determine the basic volume of capital construction in these sectors of the economy.

The course of construction of projects is considered regularly at conferences of oblast staff meetings. Special attention is given to construction projects designated as major projects of the five-year-plan by the 26th CPSU Congress. In spite of this, we must report today that operations here are extremely unsatisfactory.

All general contracting trusts such as "Turkmenkhimstroy," "Marykhimstroy," "Gaurdakhimstroy" and "Turkmenvostokneftestroy" and the sub-contracting trust "Turkmenkhimmontash" are in debt to the state. These are alarming facts. Really, why have builders of the TZAU fulfilled only one-half of their plan? Why were the UZK-3 [expansion unknown] and the PVS-350 not put into operation as scheduled in December 1981? What is delaying the orderly completion of construction volumes required at the ELOU [electric desalination unit] AVT [expansion unknown] installation in Neftesavodsk?

Directors of these collectives attribute the failure to meet the state targets to a shortage of personnel, materials and other objective difficulties. It is partly true that somewhat of a labor shortage and disruption of supply have occurred here in spite of measures taken to prevent them. The TZAU builders, for example, received very little pre-cast reinforced concrete in January for use on projects

under construction. The Chardzhou Petroleum Refining Plant did not receive enough lumber, pipes and metal. Therefore, the rebuke of "Turkmenstroykomplekt" and "Turkmenstroyindustrii" is quite justified.

However, the immediate organizers of the construction conveyor, the party committees at the sites, ministries and departments also deserve severe reproach. The latest inspection of the state of affairs at the construction projects of the sector presented a sad picture which can be depicted briefly as a state of mismanagement and poor organization of production and work.

We shall present some figures and examples. The first TZAU complex under construction for output of dilute nitric acid and ammonium nitrate should begin production next year but only 10.4 million rubles out of a budget of 34 million has been developed as yet. Rates of operations must be accelerated as much as possible and this requires, first of all, putting into operation their own production base, especially a concrete mixing plant which is badly needed now. However, there are no such bases. The management of the TuSSR Ministry of Construction and the "Marykhimstroy" trust sites have not been able to allocate the forces of the collective properly at the most important sites. The oblast staff for supervision of the construction project, the chairman of which is Deputy Chairman of the oblast Executive Committee F.A. Kazinov, did not notice the obvious error.

The site is literally heaped with materials (at the same time as there is a shortage of them). Sectional reinforced concrete lays without being used because some parts are missing. Expensive metal structures lay on the ground in disorder. In January, 1300 tons of them awaited assembly. The area is so cluttered that it is impossible to dig a foundation pit under the granulation section for which 185 tons, literally, of structural members have been delivered.

There is a simple explanation for this; there is nothing and nobody to erect the structures. The Mary SUMR [expansion unknown] did not provide the mechanisms nor the cranes. Moreover, the small amount of equipment available, frequently is broken and standing idle because Chief of the SUMR N. Seytiyev and the "Spetsstroymekhanizatsiya" trust managers did not get around to taking the initiative to ensure the proper care of the mechanisms and the repair base. Remarks in an address by N. Seytiyev and by manager of the sub-contracting SMU [Construction and Installation Administration] "Turkmenspetsystroy" trust A. Beshimov, who admitted obvious waste in the work, were made at oblast staff meetings many times. What were the conclusions and the results? There are no signs of them, regrettably.

The erectors are working poorly. Last summer, members of "Turkmenkhimmontazh" trust began assembly of the gas containers but stopped because they could not do it. They fulfilled the January quota by 48 percent. Representatives and other organizations of the USSR Ministry of Installation of Special Construction are very scarce at the project. The figure for the "Volgostal'montazh" administration is 21. There are no personnel at the "Yuzhstal'konstruktsii".

It would seem that if the personnel problem is so acute, its solution should be expedited by building more residences and by improving living and working conditions at the project. This, however, is not being done. The Mary house building combine disrupted the introduction of two 56-apartment dwelling houses for the

"Marykhimstroy" trust last year. Housing construction was slow in the first quarter. The dining room is small. Telephone service is not yet available.

Members of the oblast staff certainly should understand that the solution of important social problems provides the key of success in erection of the TZAU. However, significant efforts in the direction required are not being made. Staff meetings involve only the statement of the facts. Is this not the reason why the same points are covered over and over in the minutes of the meetings?

Persons responsible for major difficulties in the installation of the Turkmen Nitrogen Fertilizer Plant were not heard from at all in the last year at Mary Gorkom meetings. Meanwhile, demand from manager subdivisions of the TuSSR Ministry of Construction and the TPRO [Turkmen Production and Control Administration] of the USSR Minmontazhspetstroy and customer enterprises should be strict and in accordance with Party principle and this refers not only to Mary.

The point is that miscalculations in production organization, illustrated by the example of the situation at TZAU, are typical of other projects of the industry. The solutions of social problems have been set aside in the latest project in Gaurdak. Suffering from a shortage of workers, the "Gaurdakhimstroy," at the same time, is not building its own dormitory. The Chardzhou house building combine is helping. Last year, instead of the two residential buildings planned, it put only one into use and in January it did not spend a ruble on residential construction.

At the same time, in 1981, the combine greatly exceeded the quota for completion of projects in Chardzhou itself. The principle "my own shirt is nearest to my body" scarcely applies to cases involving a project of national importance. However, neither the TuSSR Ministry of Construction nor the Chardzhou obkom and oblispolkom rebuffed the local biases. They did not take a constructive approach to the solution of the Gaurdak problems. It is high time to create a permanent section for development of a workers' settlement and to reinforce here the position of the ministry and the TPRO. The PVS-350 complex was not finished on time precisely because of the weakness of their collectives.

In a word, there are more than enough reasons for operational interference of Chardzhou obkom workers in the Gaurdak affair. The enterprise faced a real threat of losing the position as a leading collective won by them. If the complex is not delivered in the first half of this year and the miners do not change to the new fourth mining section, serious complications in sulfur output will arise since supplies at the other sections are almost completely exhausted.

The only way out is for all participants in the installation of PVS-350 to work with maximum effort in order to make up, in a short time, what has been allowed to lag and to remember, of course, the schedule which was compiled last August. The TuSSR Minister of Construction N.V. Sheremet'yev and TPRO Chief A.I. Akhmedov, in collaboration with the customer have provided, in this schedule, everything needed for the most rapid completion of work on the complex. However, not one aspect of the time limits proposed has been fulfilled.

Now specialists are complaining that it is impossible to avoid rush work. It would have been possible to avoid the rush work much sooner if the Chardzhou Oblast staff for management of major construction projects in the Five-Year Plan had provided for timely fulfillment of the schedule and had demanded the strict compliance to it by contractors and if staff members had visited Gaurdak more frequently.

Regrettably, not enough attention is being given to another construction project -- the oil-refining plant in Neftezavodsk. There are reports at staff meetings of "poor work" such as that, for example, at the "Turkmenenergostroy" trust and at Minmontazhpetsstroy organizations. They are committed to better work. But then what happens?

This is what happens later. The "Turkmenvostokneftestroy" general contracting trust, wishing to speed up the matter, is assuming the function of a sub-contractor -- the "Montazhkhimzashchit" administration. It is shipping 500,000 rubles worth of metal structures to Ufa. They are then reshipped to Neftezavodsk in the form of heat-resistant panels, in large numbers. The trust is loading the railroad cars by their own efforts by working two shifts. The panels are already crowded on belt lines. G.M. Chochuya chief of "Montazhkhimzashchit" is not responding to appeals to come and begin assembly of the panels. This, thereby ties, hand and foot, another sub-contractor -- the "Neftezavodmontazh" administration and prevents it from carrying out its assignment.

The state of affairs at the installation of the TETs [heat and electric power plant] may also serve as an example. The project, costing 30 million rubles, should begin operation in 1984, but the "Turkmenenergostroy" trust has assimilated only 220,000 rubles in the last year. What is happening to the unscrupulous managers? How is the project being helped? In essence nothing is happening to the managers nor is help being provided for the project.

Briefly speaking, much has been discussed. However, somewhere they forget that deeds should follow words. It is important to turn attention to the main, decisive item which is, exactly, work with personnel.

Let us return to Krasnovodsk where a large construction project, a slow coking apparatus, is underway. In the second half of last year, oblast and municipal party committees, in collaboration with the TuSSR Ministry of Construction, succeeded in greatly increasing the rates of construction and installation operations at the site or, rather, were able to increase the volume of them. However, the delays, generated by the inactivity of the "Turkmenkhimstroy" trust in recent years have not been overcome. Equipment was not put into operation. Training persons at the site was greatly reduced.

There, the launching was brief and indecisive. Why? It seems, in the first place, basically because extensive methods of management were employed at the site. They assembled, although with delay, many people, much equipment and materials but the resources of the administration and the organization remained unused. At the final stage, the fruits of the inefficiency of the client, the board of directors of the petroleum refining plant, appeared. It became evident that revision of the technological equipment is going poorly and slowly and there are not enough persons for the start-up and adjustment work nor skilled operators.

The construction project faltered. Today only a little more than one-half of the 44 projects of the start-up complex have been accepted.

Improvement of the management method and the style of administration of the capital construction is a problem of paramount importance.

2791

CSO: 1841/179

NEW, EFFICIENT ACETIC ACID PLANT GOES ON LINE, FACES DISTRIBUTION PROBLEMS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 31 Mar 82 p 1

[Article by S. Pertsovskiy, contributor to SEVERODONETSKIY KHIK, Voroshilovgrad Oblast: "Twice as Cheap, Thrice as Productive"]

[Text] Chemists of the Northern Donets "Azot" Association imeni Lenin Komsomol have achieved the planned capacity of the largest acetic acid complex in the country three months ahead of time. Then their product was awarded the State Seal of Quality. This is the first such award which the Northern-Donets chemists have won this year.

The collective of the new complex did not spend a great amount of time on this. The outstanding training and high qualification of the workers, engineers and technicians helped in this matter. The occupational proficiency of V. Goncharov, A. Isayev, V. Lysak, L. Uzhik, N. Voronin, B. Reznik and many of their comrades was quite evident here. They attend large tonnage assemblies, units for separation of gases, reforming furnaces in which the technological process begins in the deep cold of 183 degrees below zero and continues up to plus 850 degrees with precision and without the slightest deviations. So now they are producing synthetic acetic acid for the first time in the world.

Most chemists at the new shop are graduates of secondary schools or higher technical schools and almost all have mastered related specialties. Here the results of any change in the regime must be foreseen or otherwise the situation is impossible because of the large number of cycles of different kinds, the corrosive medium and many stages of the process.

"Immediately after start-up" relates shop chief V. Zagorul'kin, "central control panel operators still worked with some allowances in technology, but this is inadmissible now that the loads have increased. Automatic systems and electronics, a new complex controlled with the use of an EVM (electronic computer), stop production if there are any variations in the process."

The new equipment may provide annually 150,000 tons of valuable raw material for chemical, pulp and paper, perfumery, pharmaceutical and some other sectors of industry.

The production level already has exceeded the required standards, and it is noted constantly on shop "quality monitors" that the level of the basic substance in the finished acid reaches 99.8 % or more (while the standard requirement is 99.7 %).

It is no accident that FRG and Finnish firms gladly buy the Northern Donets acetic acid and that it is exported to Czechoslovakia, Hungary and Bulgaria.

One of the basic factors which ensure acceleration of work at the new complex is the assistance of USSR Academy of Sciences scientific Institutes of Chemical Physics and Organic Chemistry and the UkSSR Academy of Sciences Institute of Electric Welding imeni Ye. O. Paton.

"The new complex will pay for itself in only 2.5 years," reports the association director B. Lishina, delegate to the 26th CPSU Congress. "We have used for the first time in the country a large scale method of carbonylation of methanol in which the product is produced not as a result of long conversions of raw material in several shops, but actually under one roof, as a result of the interaction of only two components. It is possible to unload the finished product only 4 or 2.5 hours after feeding the raw material into the reactor. At old facilities the cycle lasts for an entire shift or even 12 hours. Naturally, the production cost of our acetic acid is reduced by 50% and labor productivity is increased three-fold."

It is also quite important that the new equipment ensures practically complete use of wastes and does not harm the environment. The hydrogen which is a waste product in this operation will be used in other shops of the association.

Of course, problems still exist. It seems that some users, especially the Fergana "Azot" Association, the Mogilev "Khimvolokno" Association and the Amzra Wood Chemistry Plant still cannot accommodate such a large amount of raw material, although they sent "rush" orders quite recently. There is a great shortage of special containers. Rolling stock used to ship the product is often kept by the users who turn it into warehouses on wheels, whereas it would be more economical to build permanent containers. Evidently, the Ministry for Production of Mineral Fertilizers should help here.

Actually, the situation is becoming paradoxical. Acetic acid is very necessary to industry while the largest producer quite frequently is operating at only two-thirds of its capacity. We have become accustomed to saying that consumers should be registered with actual suppliers, but here there is now a need to achieve exactly the opposite.

2791

CSO: 1841/179

UDC 658.511.2 : 669.2/8

ECONOMIZING ON NON-FERROUS METALS AND ALLOYS

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 4,
Apr 82 pp 5-6

VASIL'YEV, A. M., candidate of technical sciences, member of the collegium,
Ministry of Chemical Machinebuilding

[Abstract] To economize on non-ferrous metals such as aluminum, titanium, copper, bronze, lead and brass used in chemical and petroleum machinery, attempts have been concentrated on using substitute materials in laminates and other applications. Hot stamping and powder metallurgy have been used in making screws, spindles and housing. Pipe fittings are being made by pressure casting processes. Products formerly made of nickel alloyed stainless steels are using less nickel (decreasing from 10% to 2-6%); other alloys are also being utilized that economize on deficit metals. Improved enamel coatings permit use of lower-grade steels in many corrosive environments. Metal cutting devices are being designed that economize on tungsten. Copper laminations for chemical equipment, brass and aluminum use have all been reduced. Major tasks remain in sparing non-ferrous metals in equipment for petroleum and natural gas shipping where these energy sources have high hydrogen sulfide content. Other applications of laminated metals offer additional prospects for economizing.

[182-12131]

UTILIZING PLASTICS AND FIBER GLASS INSTEAD OF STAINLESS STEELS AND NON-FERROUS METALS FOR CHEMICAL EQUIPMENT

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 4,
Apr 82 pp 9-11

SEVEROV, G. F., POSYSOYEVA, A. P. and LITVINENKO, A. F., engineers

[Abstract] Plastics, synthetic resins and related materials are being used for chemical containers and various filters for separating suspensions. Filters have been made in drum, strip, plate and carousel forms for vacuum and pressure filtration. Plate and frame filters with hand loading and automatic unloading have been made to replace earlier stainless steel versions. The Northern Donetsk Branch of the Scientific Research Institute for Chemical Machinery has developed press filters of thermoplastics that improve the cleanliness of filtered products, increase corrosion resistance and reduce both the mass of the product and the labor involved in producing it. Polyethylene press filters are being made for aniline-dye and chemical and pharmaceutical applications. Screw-drive plastic loaders to withstand temperatures to 120° C are being produced of polyethylene, polypropylene and other thermoplastics, and chemical containers of 0.8 to 10 cubic meter volume are produced from fiber glass. A fiber glass vacuum drum filter is being made to replace rubber-coated steel versions. All of these applications offer financial benefits and economize on deficit domestic raw materials. Figures 4; references 3 (Russian).
[182-12131]

UDC 621.793.7"313"

PROSPECTS FOR USING GAS-THERMAL SPRAY COATINGS IN PETROLEUM AND CHEMICAL MACHINE BUILDING

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 4,
Apr 82 pp 13-14

AFANASENKO, Ye. A., engineer, SHESTAKOV, A. I., candidate of technical sciences, and SLOBODYANIKOV, B. A., engineer

[Abstract] Durable and corrosion-resistant coatings allow reduced metal consumption for spare parts, thus increasing production of machines and equipment. Sprayed coatings are porous and lack durability, and the authors have studied various methods to improve these parameters. Plasma spray and acetylene detonation coating were tested. The sprayed material was applied either as fibers or as a powder, with 40-100 mcm diameter particles. The main drawback of detonation coating was the noise level of production, so plasma spray coating was further studied with special powder made of aluminum

coated with nickel. Self-fluxing Ni-Cr-B-Si powders were also used. Use of deficit nickel is justified in coatings partially because of the durability nickel provides. Various practical applications of plasma spray metal coatings by gas-thermal methods are being used, although delamination of nickel coatings still presents difficulty. Figures 2; references 6 (Russian).
[182-12131]

COMBUSTION

UDC 677.4.017.56:536.468+678.01:536.468

RATE OF FLAME PROPAGATION IN FABRICS OF DIFFERENT COMPOSITION

Moscow KHIMICHESKIYE VOLOKNA in Russian No 1, Jan-Feb 82
(manuscript received 10 Jun 81) pp 41-42

ZHEVLAKOV, A. F., GROSHEV, Yu. M., YERMAKOVA, I. S., VOLOKHINA, A. V.,
ZHARKOVA, M. A. and SHCHETININ, A. M.

[Abstract] The rates of propagation of flame in fabrics of different composition were investigated with different oxygen content in the gas flow. The rates of flame propagation were determined with the fabric specimen burning from top to bottom. The experiments were carried out in atmospheric air on a device designed to determine the oxygen index. The rates of flame propagation are different for the investigated materials. Materials which burn practically without flame in the form of smoldering showed the lowest rate of flame propagation. The combustion point increased with an increase of oxygen content in the gas flow and as a result the heat flux on the unburned part of the specimen and also the rate of flame propagation increased. Figures 1; references 9: 4 Russian, 5 Western.
[148-6521]

UDC 614.841.415

CRITERION FOR EXTINGUISHING FIRES WITH COOLING FIRE EXTINGUISHERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEVA
in Russian Vol 27, No 1, Jan-Feb 82 pp 11-17

ABDURAGIMOV, I. M., professor, doctor of technical sciences, head of Chair of Combustion Processes, Higher Engineering Firefighting School, USSR Ministry of Internal Affairs

[Abstract] Soviet and foreign literature is surveyed on problems of developing criteria for extinguishing fires and for optimizing the quantitative indicators of efficiency and quality of extinguishing certain types of fires.

The conditions that are necessary and adequate to stop diffusion combustion of gaseous, liquid and solid hydrocarbon fuels from burning are outlined. The quantitative expression of the criterion for extinguishing ordinary fires and the indicators of the effectiveness and quality of extinguishing them are considered in detail. Examples of using the derived criteria are presented for calculating the main parameters of the process of fire extinguishing. Figures 4; references 15: 9 Russian, 6 Western.
[159-6521]

UDC 628.741:622.323

FIREFIGHTING ENGINEERING PROBLEMS OF STORING LIQUIDS IN TANKS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 36-40

VOLKOV, O. M., candidate of technical sciences, docent, deputy chief of Chair of Fire Prevention in Production Processes of Plants, Higher Engineering Firefighting Engineering School, USSR Ministry of Internal Affairs

[Abstract] The current state of firefighting engineering problems of storage of oil, petroleum products and other flammable and fuel liquids in tanks is outlined from materials of Soviet and foreign papers. The results of estimating the flammability of tanks in typical states such as those normally operating, those protected and being repaired, openly burning tanks, those heated by a fire and those with burning in the openings are considered. The characteristic features of the flammability of new large-capacity tanks are noted and the three basic directions of investigations are given. Figures 2; references 21: 17 Russian, 4 Western.
[159-6521]

UDC 614.83:66.074.48

DISCHARGE OF GASES AND VAPORS FROM EQUIPMENT UNDER EMERGENCY CONDITIONS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 61-66

EL'NATANOV, A. I., candidate of chemical sciences, senior scientific worker, State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis

[Abstract] The methods and procedures for rational discharge of gases and vapors from equipment during emergency situations that arise at chemical and petrochemical enterprises are considered. The main requirements are formulated that are placed on controlled discharge and product gathering systems for open burning. Laboratory and full-scale determination of the effect of

gas and vapor discharge on people and the environment are studied. Practical recommendations are presented on the basis of existing norms and regulations to ensure safety in discharge of these products. References 21: 12 Russian, 9 Western.
[159-6521]

UDC 541(126+127)

NEUTRALIZATION OF WASTES FROM CHLOROORGANIC PLANTS BY BURNING

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 67-72

MAL'TSEVA, A. S., candidate of technical sciences, senior scientific worker, GOSNIIKhLORPROYEKT, FROLOV, Yu. Ye., laboratory head, GOSNIIKhLORPROYEKT, and ROZLOVSKIY, A. I., doctor of chemical sciences, senior scientific worker, GOSNIIKhLORPROYEKT

[Abstract] Unutilized chlorine derivatives from the chemical industry are neutralized by burning. It is assumed that all the bound chlorine is converted to hydrochloric acid which is then absorbed by water. Hydrochloric acid is utilized at some plants in the form of the acid or by oxychlorination; neutralization by burning at sea is also widespread with the products being absorbed by sea water. Almost all the bound chlorine can be broken down by neutralization through burning. However, a considerable part of it is converted to the elementary state and to phosgene. The fraction of conversion to chlorine reaches 18 percent for carbon tetrachloride and it reaches from 1.5 to 6 percent in COCl_2 . It is difficult to completely neutralize these products by water. Neutralization of fuel chlorohydrocarbons is very difficult without additional fuel. This fact makes neutralization of chlorine derivatives by burning ecologically unacceptable. References 53: 16 Russian, 37 Western.
[159-6521]

UDC 661.716.242:658.332.3

PRODUCTION SAFETY AND REFINING OF ACETYLENE

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 73-80

STRIZHEVSKIY, I. I., laboratory head, State Scientific Research and Planning Institute of the Nitrogen Industry and Products of Organic Synthesis

[Abstract] The explosive properties of acetylene, means of localizing the breakdown of acetylene and the flame of acetylene-oxygen mixtures and also conditions for safe operation of compressors for compressing acetylene to

$26 \cdot 10^5$ pascals were investigated. Acetylene is the most explosive of all gases used in industry due to its high endothermicity and nonsaturation nature. A device for emergency closing of high-pressure acetylene pipelines is described. The valves are closed by springs arranged radially around the enclosing shaft. Other safety devices include piston servo mechanisms, electric devices, fire barricades for fuel gas signalling devices and tower fire barricades for low- and medium-pressure acetylene pipelines. The safety features of piston compressors for compression of acetylene, the safety of acetylene solutions in liquid ammonia and the safety of acetylene solutions in acetone are given. Figures 6; references 25: 15 Russian, 10 Western.
[159-6521]

UDC 541.127

REGISTRATION OF HO_2 RADICALS IN RAREFIED HYDROGEN-OXYGEN FLAME BY LMR METHOD

Moscow KINETIKA I KATALIZ in Russian Vol 23, No 1, Jan-Feb 82
(manuscript received 18 Aug 81) pp 244-245

AZATYAN, V. V., GAGANIDZE, K. I., KOLESNIKOV, S. A. and TRUBNIKOV, G. R.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] Experimental conditions have been described for direct registration of HO_2 radicals by the laser magnetic resonance method (LMR) in the gaseous phase of a rarefied hydrogen-oxygen flame between the first and second self-ignition limits. The flame was obtained in an electrically heated quartz tube in form of a stream. After emergence from the tube the gas stream passed through the LMR registration cuvette. The flame temperature ranged from 873 to 923 K, with gas pressure of 10-25 mm Hg and the $\text{O}_2:\text{H}_2$ ratio varying from 4:1 to 1:2. The velocity of the gas stream was 20 m/s. Concentration of HO_2 radicals in the registration cuvette was about 10^{13} cm^{-3} . The spectrum obtained was identical with the spectrum reported in an earlier study. References 9: 7 Russian, 2 Western.
[170-7813]

UDC 665.753.2:542.943:541.127

KINETIC PRINCIPLES OF HYDROPEROXIDE DEGRADATION IN JET FUELS

Moscow NEFTEKHIMIYA in Russian Vol 21, No 6, Nov-Dec 81
(manuscript received 8 Jan 80) pp 909-914

KOVALEV, G. I., ZVEREVA, N. S. and DENISOV, Ye. T.

[Abstract] Hydroperoxides break down in T-6 and RT jet fuels by a first-order reaction and the values of the rate constants of the breakdown is one

to two times greater than the corresponding values for individual peroxides in inert solvents. The activation energy of the breakdown of individual hydroperoxides is 125-170 kJ/mole, which corresponds to the breakdown energy of the molecule and oxygen-oxygen bond. The activation energy is 74-76 kJ/mole in jet fuels. The effectiveness of initiation of hydroperoxides in T-6 jet fuel is 0.04-0.06 and that in RT jet fuel is 0.015-0.020, which is lower than the cellular effect. Figures 3; references 3 (Russian).
[95-6521]

UDC 547.21:665.74:542(941.952)

HYDROISOMERIZATION OF n-PARAFFINS OF KEROSENE WITH HIGH SULFUR CONTENT

Moscow NEFTEKHIMIYA in Russian Vol 21, No 6, Nov-Dec 81
(manuscript received 25 May 81) pp 915-923

KHALIL', F. G., AYYAD, S. and FRANCIS, G., Egyptian Research Institute, Cairo

[Abstract] Using the example of directly distilled high-sulfur kerosene from the Morgan petroleum deposit in Egypt, jet fuel was produced by hydroisomerization of n-paraffins contained in the fraction without preliminary separation. Hydroisomerization of paraffin-naphthene kerosene with high sulfur and nitrogen content can be used to produce jet fuel from it. Kerosene fractions with boiling point of 150-250°C were hydroisomerized on nickel oxide deposited on clay at 350°C and at hydrogen pressure of 5 MPa. The yield of isomers from n-paraffins is 39 percent. Preliminary treatment of the kerosene with concentrated sulfuric acid at the rate of 3 percent by mass yields a more suitable raw material to produce jet fuel using the hydroisomerization process. The results are promising with respect to jet fuel production by direct hydroisomerization of kerosene distillates with minimum cracking. References 21: 8 Russian, 13 Western.
[95-6521]

EXPLOSIVES AND EXPLOSIONS

UDC 614.838:62-5

NEW MEANS OF AUTOMATIC SUPPRESSION OF EXPLOSIONS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 3-10

VODYANIK, V. I., head of Laboratory of Explosion Protection of Production Equipment, All-Union Scientific Research Institute of Safety Engineering in the Chemical Industry

[Abstract] Engineering the advantages of automatic systems for suppression of explosions in equipment are shown compared to devices that drop explosive pressure. The dynamics of an explosion developing in a closed space are described and requirements are formulated on this basis for automatic explosion-suppression systems. The design and operating principle of the basic elements of systems such as explosion indicators, explosion suppressors and high-speed flame extinguishers are described. The interaction of a flame-suppressing composition with combustion focal area is considered and the optimum methods of spraying the flame-suppressing composition are described. Examples of using automatic explosion-suppression systems are given and the most promising areas for their use in the chemical industry are shown. Figures 5; references 21: 13 Russian, 8 Western.
[159-6521]

UDC 614.841.34:66

PROBLEMS OF ENSURING EXPLOSION SAFETY OF CHEMICAL PLANTS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 22-29

BARATOV, A. N., doctor of technical sciences, deputy chief of All-Union Scientific Research Institute of Firefighting Defense, USSR Ministry of Internal Affairs

[Abstract] The state of problems of categorizing industrial facilities for explosion hazards and also for determining the combustion limits are

analyzed from a critical viewpoint. It is noted that the existing standard method of determining the combustion limits when testing slowing burning materials may provide unreliable results. Free convection sometimes has a significant effect on spreading of flame of new-limit mixtures. The range of combustion of carbon-containing materials is expanded as the pressure increases. The existing principles and criteria for categorizing facilities for explosion hazards have not been adequately perfected. New principles of categorization based on thermodynamic calculation of the explosive load and the difference between the flash point and the temperature of the surrounding medium, are proposed. Figures 7; references 36: 29 Russian, 7 Western.
[159-6521]

UDC 66.013.004.6

QUANTITATIVE ANALYSIS OF HAZARDS AND METHODS OF EXPLOSION PROTECTION OF
CHEMICAL PRODUCTION PROCESSES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEVA
in Russian Vol 27, No 1, Jan-Feb 82 pp 41-48

BESCHASTNOV, M. V., chief engineer, Administration for Inspection in the
Chemical Industry, USSR State Committee of the Council of Ministers for
Supervision of Industrial Safety and for Mining Inspection

[Abstract] Quantitative indicators for estimating the flammability of chemical production processes are proposed on the basis of analysis and generalization of the causes of accidents and processing of statistical data. The indicators take into account the energy potentials of the flammability of production processes, the properties and state of flammable and fuel-handling materials, the nature and equipment formulation of processes, specific causes of unsealing of production systems and sources of combustion. A method of estimating the flammability of chemical production processes was proposed which was tested in many real industrial chemical production processes. Efficient engineering solutions of explosion protection are determined from the generalized indicators. References 36: 35 Russian, 1 Western.
[159-6521]

EXPLOSION HAZARD OF PLANTS OF CHEMICAL INDUSTRY RELATED TO HANDLING OF FUEL GASES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 57-60

STREL'CHUK, N. A., professor, doctor of technical sciences, rector of Moscow Construction Engineering Institute imeni V. V. Kuybyshev, PCHELINTSEV, V. A., candidate of technical sciences, senior scientific worker, Moscow Construction Engineering Institute imeni V. V. Kuybyshev, NIKITIN, A. G., candidate of technical sciences, head of Laboratory of Industrial Buildings and Structures, Moscow Construction Engineering Institute imeni V. V. Kuybyshev, and RABINKOV, V. A., junior scientific worker, Moscow Construction Engineering Institute imeni V. V. Kuybyshev

[Abstract] The conditions for formation of explosive-hazardous gas-air mixtures during leaks of fuel gases into production buildings are considered. The same gas may represent a different hazard with respect to the formation and volume of explosion-hazardous mixture with identical intensity of its entry into a building. This factor should be taken into account when evaluating the explosion hazard of plants and when working out solutions for disposition of equipment to ensure explosion safety. References 13: 11 Russian, 2 Western.

[159-6521]

DETERMINATION OF VOLUME OF EXPLOSIVE GAS MIXTURE DURING CATEGORIZATION OF PLANTS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 81-84

MAKEYEV, V. I., candidate of technical sciences, chief of laboratory, All-Union Scientific Research Institute of Fire Prevention, MONAKHOV, V. T., candidate of technical sciences, and PLESHAKOV, V. F., chief engineer, "Kriogenmash" Scientific Production Association

[Abstract] A physical mathematical model for the formation of a gas-air cloud during instantaneous discharge of gas into an inorganic space was investigated. Data are presented on the parameters of the explosion and fire hazard of volumes of gas-air mixture capable of explosion, the time of existence of an explosion hazard and the dimensions of explosion-hazardous zones on the basis of analytical solution of the problem and experimental results. Numerical values of the coefficient that takes into account the nonuniform filling of an explosive volume with fuel gas were derived for use in calculating the volume of an explosive mixture in categorization of plants. Figures 4; references 7: 5 Russian, 2 Western.

[159-6521]

FERTILIZERS

UDC 661.525:66.092.1

ENVIRONMENTAL SAFETY AND PROTECTION DURING PRODUCTION OF AMMONIUM NITRATE
AND FERTILIZERS BASED ON IT

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IMENI D. I. MENDELEYEVA in Russian Vol 27, No 1, Jan-Feb 82 pp 49-57

STRIZHEVSKIY, I. I., head of Laboratory, State Scientific Research and
Planning Institute of the Nitrogen Industry and Products of Organic
Synthesis

[Abstract] The thermal breakdown of ammonium nitrate, the process of producing ammonium nitrate in large units, the fire and explosion hazardous properties of fertilizers containing ammonium nitrate and processes of scrubbing gaseous discharges were investigated. Granulated ammonium nitrate used as fertilizer can detonate but requires large explosive charges for initiation at ordinary temperatures. Fertilizers containing ammonium nitrate are classified in four groups. Group A includes ammonium nitrate and mixtures of it capable of detonation transformation, Group B includes mixtures containing ammonium nitrate capable of spontaneous distribution of thermal decomposition, Group C includes mixtures containing ammonium nitrate incapable of spontaneous distribution of thermal breakdown or detonation transformation and Group D includes mixtures which are safe in aqueous solution or in suspension, but are capable of detonation in crystalline form. The temperature of ammonium nitrate in bags or in bulk form should not exceed 55°C in a warehouse. It should be stored in single-story warehouses of second degree of fire resistance. Figures 1; references 33: 16 Russian, 1 Polish, 16 Western.
[159-6521]

ION EXCHANGE PHENOMENA

UDC 541.183

CHANGE OF ION EXCHANGE PROPERTIES OF VPK AMPHOLYTE IRRADIATED IN FORM OF INTRAMOLECULAR SALT

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 2, Feb 82
(manuscript received 9 Feb 81) pp 369-371

TABAKOVA, S. V., KISELEVA, Ye. D. and CHMUTOV, K. V. (deceased), Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] The chemical properties of VPK (vinylpyridinecarboxylate) ampholyte undergo drastic changes when placed in different media: in basic solvent they exist as cation exchange resins, in strong acids—as anion exchange resins and in neutral or weakly acidic medium they are found in the form of an intramolecular salt. The most suitable form for the study of VPK radiolysis is that of the intramolecular salt in an acetate buffer. The effect of ionizing radiation on VPK ampholyte was investigated in acetate buffers containing 0.1 M CH_3COOH , 0.1 M CH_3COONa and NaNO_3 salts. It was found that irradiation of VPK led to decarboxylation, breaking of the crosslinkage and oxidation of the ion exchange resin. Addition of NaNO_3 to the irradiated solution protected the macromolecular structure. The most resistant form of VPK to radiation is that of an intramolecular salt. Figures 2; references 6 (Russian).
[162-7813]

UDC 541.183

CHANGE OF ION EXCHANGE PROPERTIES OF VPK AMPHOLYTE IN COMPLEX FORM DURING IRRADIATION

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 2, Feb 82
(manuscript received 9 Feb 81) pp 372-375

TABAKOVA, S. V., KISELEVA, Ye. D. and CHMUTOV, K. V. (deceased), Institute of Physical Chemistry, USSR Academy of Sciences, Moscow

[Abstract] The VPK ampholyte (vinylpyridinecarboxylate) forms strong complexes with many metals. The effect of ionizing radiation was studied

on VPK samples partially filled with Sr^{2+} , Pr^{3+} and UO_2^{2+} ions. The radiation effect was found to be identical in all cases. The metal complexes protected the carboxyl group from breakdown; the complexes remained intact and none of the ions tested were found in solution. Maximum absorption of metal ions on the ampholyte led to total protection from breakdown of the carboxyl groups due to irradiation. However, the crosslinking bonds of the sorbent were broken. Evidently the absorbed energy is principally localized on the weaker COOH bonds and on the sorbent crosslinking bonds. Figures 2; references 9: 8 Russian, 1 Western.
[162-7813]

NITROGEN COMPOUNDS

UDC 547.779.1'81.07

SYNTHESIS AND SOME CONVERSIONS OF 4H-PYRANO[3,2-d]PYRAZOLES

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, Mar 82
(manuscript received 6 Jan 81) pp 317-320

MITYURINA, K. V., KHARCHENKO, V. G. and CHERKESOVA, L. V., Saratov State University imeni N. G. Chernyshevskiy, Saratov

[Abstract] In a new reaction that produced 4H-pyrano[3,2-d]pyrazoles, 4-(3-oxopropyl) pyrazolones were found capable of cyclization into pyranopyrazoles of varying structure with the aid of polyphosphoric acid without solvents when there was an excess of polyphosphoric acid and 60-80° C temperature. Use of alcohol or acetic acid as a solvent retarded the process. The chief features of the pyranopyrazoles' chemical behavior were stability and inertness in salt formation with perchloric acid in acetic anhydride and in Leicart and Chichibabin reactions. An ion hydrogenation reaction not involving the double pyrane bond proceeded successfully to form 5,6-dihydropyrano[3,2-d]pyrazoles. Phosphorus polysulfide in xylol reacted with the pyranopyrazoles to form a salt containing a complex anion made up of dihydrophosphate, dihydrothiophosphate and dihydrodithiophosphate of pyrazolo[5,4-b]thiapyrilium. Reactions with phosphorus polysulfide in various solvents brought formation of various products containing sulfur through an intermediate pyrane stage. Structures were confirmed through proton magnetic resonance. Details of procedures used are presented in the experimental section. References 12: 5 Russian, 7 Western.
[181-12131]

CHEMISTRY OF ISOFLAVONE HETEROANALOGS, PART 9: INTERACTION OF ISOFLAVONE THIAZOLE ANALOGS WITH NUCLEOPHILIC AND ELECTROPHILIC REAGENTS

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, Mar 82
(manuscript received 27 Dec 80) pp 321-327

KHILYA, V. P., KUPCHEVSKAYA, I. P., KAZAKOV, A. L., TKACHUK, T. M. and
GOLUBUSHINA, G. M., Kiev State University imeni T. G. Shevchenko, Kiev

[Abstract] Reactions of thiazole analogs of isoflavones with hydrazinehydrate, methylhydrazine, phenylhydrazine and hydroxylamine readily led to regrouping into derivatives of 2-hydroxyphenyl)pyrazole and pyrazole isomers. Earlier related studies, showing an oxime structure resulting from the reactions of chromones, flavones and isoflavones with hydroxylamine, were shown to be incorrect, with the actual compounds formed being isoxazole isomers. Mixtures of the latter were separated into the individual compounds by selective crystallization and thin-layer chromatography. Details of chromatography aid in identifying individual compounds. Cardiovascular medicinal applications of isoflavone heteroanalogs were studied, and it was learned that several of the title compounds controlled the development of hyperlipidemia, and reduced cholesterol and triglycerides. Details of procedures used are given in the experimental section. References 14: 6 Russian, 1 Hungarian, 1 Polish, 6 Western.

[181-12131]

SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES, PART 33:
SYNTHESIZING 1,3,4-OXADIAZOLES CONTAINING INDOLYL RADICAL

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, Mar 82
(manuscript received 4 Feb 81; after revision 15 Jul 81) pp 343-347

KELAREV, V. I. and SHVEKHGEYMER, G. A., Moscow Institute of Petrochemical
and Gas Production imeni I. M. Gubkin, Moscow

[Abstract] Continuing study of the synthesis and conversions of iminoether hydrochlorides, the authors studied the latter's reactions with certain hydrazides to obtain corresponding 1,3,4-oxadiazoles that are little known. Condensation of iminoether ethyl hydrochlorides of 3-indolcarboxylic and 3-indolylacetic acids with hydrazides produced corresponding 2,5-disubstituted 1,3,4-oxadiazoles containing indole residues. A similar reaction using hydrazides of the two acids produced lesser yields. A former method using carboxylic acids and hydrazine salts in the presence of polyphosphoric acid was shown to be capable of synthesizing symmetrical indolyloxadiazoles from the corresponding indole acids. Structural results were confirmed by

proton magnetic resonance. Details of the procedures are given in the experimental section. References 7: 3 Russian, 4 Western.
[181-12131]

UDC 547.785.5.07

SYNTHESIS AND DERIVATIVES OF IMIDAZO[1,2-a]IMIDAZOLE

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, Mar 82
(manuscript received 14 May 81) pp 384-387

IVASHCHENKO, A. V., LAZAREVA, V. T., SHMELEV, L. V. and POPONOVA, R. V.,
Scientific Research Institute for Organic Intermediate Products and Dyes,
Moscow

[Abstract] Continuing the synthesis and study of derivatives of 1(7)H-imidazo 1,2-a imidazole reported earlier, the authors produced 1(7)H-imidazo[1,2-a]imidazoles through reduction of 1-benzylideneaminoimidazo[1,2-a]imidazoles with zinc in acetic acid. The title compounds partially form corresponding N-oxides when separated from the reactive mass. The composition and structure of the synthesized compounds were confirmed by element analysis and electron, infra-red, X-ray electron, proton magnetic resonance and mass spectrography. The PMR spectra of the compounds in the reaction show aliphatic, aromatic and NH protons, while, after separation, ortho-proton signals of a phenyl ring were observed. The effect of nitrous acid on 1-amino-3,6-diphenyl-2,5-dipropylimidazo[1,2-a]imidazole brought formation of an N-oxide and not of 1H-imidazo[1,2-a]imidazole, as previously reported (KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY No 9, Sep 73 p 1190). Details of the procedures used are given in the experimental section. References 4 (Russian).
[181-12131]

UDC 547.821'853 : 541.6

CHEMICAL PROPERTIES OF AZINEYLIDENE DERIVATIVES, PART 1: STRUCTURE OF PROTONIZATION PRODUCTS OF DIHYDROPYRIMIDYLIDENE-2- AND -4-CYANACETIC ESTERS

Riga KHIMIYA GETEROTSIKLICHESKIKH SOYEDINENIY in Russian No 3, Mar 82
(manuscript received 29 Jun 81) pp 397-404

ZAGULYAYEVA, O. A., GRIGORKINA, O. A., MAMATYUK, V. I. and MAMAYEV, V. P.,
Novosibirsk Institute of Organic Chemistry, Siberian Branch, USSR Academy
of Sciences

[Abstract] Initial esters were synthesized by a heteroarylation reaction of Na-cyanoacetic esters with corresponding chloropyrimidines. Because of

the instability of 4-chloropyrimidine, an unsubstituted 3,4-dihydropyrimidylidene-4-cyanoacetic ester was obtained by catalytic dechlorination of 6-chloro-3,4-dihydropyrimidylidene-4-cyanoacetic ester. The structures of the products obtained are confirmed by infrared, ultraviolet and proton magnetic resonance spectra. The data thus obtained did not rule out partial protonization with the formation of aromatic structures, which were rapidly converting with the unprotonized form. An example of the latter occurs with 1,2-dihydropyridylidene-2-cyanoacetic ester in a CF_3COOH solution. More precise structural confirmation was obtained by using nuclear magnetic resonance of ^{13}C . Data indicated that dihydropyrimidylidene cyanoacetic esters that were analogous to enaminoketones were polar compounds with pronounced charge alternations in the neutral molecule and the cation. NMR data enabled calculation of the degree of protonization in mediums of varying acidity, and led to the overall conclusion that in contrast to corresponding alpha-derivatives of pyridine, in strong acid solutions and as perchlorates, the title esters have ilidene structures. Details of the procedures used are given in the experimental section. References 15: 6 Russian, 9 Western. [181-12131]

UDC: 542.91:547.796.1

SYNTHESIS OF TETRAZOLES FROM CYANOESTERS AND ORGANIC AZIDES UNDER HIGH PRESSURE CONDITIONS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 16 Jun 81) pp 640-645

KRAYUSHKIN, M. M., BESKOPYL'NYY, A. M., ZLOTIN, S. G., SON, V. V., VAYNBERG, N. N., LUK'YANOV, O. A. and ZHULIN, V. M., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] It was earlier shown that phenylcyanate, which does not react with organic azides at atmospheric pressure, does react with benzylazide under high pressure conditions, forming N-benzyl-5-phenoxytetrazole with good yield. The purpose of this work is to determine the area of application of the reaction, its regiodirectivity and to establish the variation of its speed with pressure. The initial nitriles used were cyanoesters of phenol and its 4-methyl-, 4-methoxy-, 4-bromo-, 4-chloro-, and 4-nitro derivatives, as well as the cyanoester of β, β, β -trichloroethanol. Benzylazide, phenylazide and cyclohexylazide were used as the azide components. The main products of the reaction at 10 kbar and 105°C are derivatives of 1-benzyl-5-phenoxy-tetrazole. Yield 74-97%. The regioselectivity observed is a result of the orienting effect of orbital and electrostatic interactions. References 14: 5 Russian, 9 Western. [184-6508]

SYNTHESIS OF ISOMERIC 3(4)-NITRO-4(3)-PHENYLFUROXANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 1 Sep 81) pp 646-649

MAKHOVA, N. N., OVCHINNIKOV, I. V., KHASAPOV, B. N. and KHMEL'NITSKIY, L. I.,
Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences,
Moscow

[Abstract] This work was undertaken to determine the possibility of existence of 3-nitro-4-phenylfuroxane. The latter was produced by oxidation of 3-amino-4-phenylfuroxane with trifluoroperacetic acid in methylene chloride. The product synthesized is the first 3-nitro derivative of furoxane produced in the laboratory. The presence of the N-oxide atom of O next to the amino group is found to have a significant influence on the reactivity of amino furoxanes in oxidation. References 7: 1 Russian, 6 Western.
[184-6508]

ORGANOMETALLIC COMPOUNDS

UDC 546.05.98.18.18.33.34

SYNTHESIS OF DOUBLE LITHIUM, SODIUM AND PALLADIUM PYROPHOSPHATES

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 2, Feb 82
(manuscript received 17 May 81) pp 302-304

SOKOLOVA, I. D., MARKINA, I. B. and SHAPLYGIN, I. S., Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR Academy of Sciences

[Abstract] Double lithium, sodium and palladium pyrophosphates— $\text{Li}_2\text{PdP}_2\text{O}_7$ and $\text{Na}_2\text{PdP}_2\text{O}_7$ —were produced by the solid-phase reaction method and their properties were studied. The quantitative rate of reaction was judged by the loss of mass of the initial mixture and the constant mass of the final product during heat treatment. The loss of mass by the reaction mixture due to removal of gaseous products was close to the calculated loss of mass for the initial reaction. Infrared spectra of the products confirmed the presence of pyrophosphate groups in them. Comparison of the X-ray diffraction patterns obtained for lithium and sodium pyrophosphates to the X-ray diffraction patterns of powders of previously synthesized $\text{K}_2\text{NiP}_2\text{O}_7$, $\text{K}_2\text{CdP}_2\text{O}_7$ and $\text{K}_2\text{CaP}_2\text{O}_7$ does not indicate any similarity in the structures of these compounds. Figures 2; references 8: 2 Russian, 6 Western. [132-6521]

UDC 541.9+541.6

COORDINATION COMPOUNDS OF METALS AND CYANOACETYLHYDRAZINE

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 27, No 2, Feb 82
(manuscript received 25 Mar 81) pp 402-406

MACHKHOSHVILI, R. I., MITAISHVILI, G. Sh. and PIRTSKHALAVA, N. I., Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR Academy of Sciences

[Abstract] The complex compounds $\text{M}(\text{NCAH})_3\text{X}_2$, $\text{M}(\text{NCAH})_2(\text{NCS})_2$, $\text{M}(\text{NCAH-H})_n$ ($\text{M} = \text{Cu, Zn, Cd, Co and Ni}$, $\text{NCAN} = \text{NCCH}_2\text{CONHNH}_2$, $\text{X} = \text{Cl, } 1/2\text{SO}_4$ and $n = 2$ or 3) were produced upon reaction of copper, zinc, cadmium, cobalt and nickel chlorides, sulfates and thiocyanates and also

[Co(NH₃)₅Cl]Cl₂ with cyanoacetylhydrazine. The properties and infrared absorption spectra of the synthesized compounds were studied and the complex Co(NCAH)₂(NCS)₂ was investigated by the X-ray diffraction method. The infrared absorption spectra of the synthesized compounds and some of their deuterium analogs were studied (with respect to the NH or ND bonds) to determine the methods of coordination of cyanoacetylhydrazine molecules in different tautomeric forms and also to study the structure of cyanoacetylhydrazine complexes of metals. Figures 2; references 7 (Russian). [132-6521]

UDC 547.258.11

REACTION OF ORGANOTIN ACETYLENES WITH ORGANIC HALIDES OF TIN

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 26 Aug 81) pp 452-453

KOMAROV, N. V., ANDREYEV, A. A. and SENICHEV, V. S.

[Abstract] A study was made of the reaction of organotin acetylenes with dihalides of dialkyl tin as a possible way of synthesizing substances with the general formula $XR_2SnC\equiv CR' + R_2SnX_2 \rightarrow XR_2SnC\equiv CR' + R_3SnX$, where $R' = H, C_4H_9, C_6H_5, Sn(C_2H_5)_3$ and $R'' = CH_3, C_2H_5$ and $X = Cl, Br$. With bis(triethyl tin) acetylene the reaction takes place with the participation of both $(C_2H_5)_3Sn$ groups and results in the formation of bis(halogen diethyl tin) acetylenes. The polymer $[(CH_3)_2SnC\equiv C]_n$ is produced when bis(triethyl tin) acetylene reacts with dimethyldichloro tin. Dialkylchloro tin acetylenes are highly reactive compounds and split easily at the $Sn-C_{sp}$ bond under the influence of water. Bis(diethylchloro tin) acetylene was obtained by heating in a sealed ampoule at 139 °C for 1.5 h a mixture of 15.3 g of diethyldichloro tin and 13.4 g of bis(triethyl tin) acetylene. After cooling, the precipitated crystals were filtered off and recrystallized from hexane. The yield of the product was 73 percent and it had a melting point of 92 °C. Bis(diethylbromo tin) acetylene was produced similarly from 13.4 g of diethyldibromo tin and 8.7 g of bis(triethyl tin) acetylene. Polydimethylstannyl acetylene was produced from 4.40 g of dimethyldichloro tin and 4.36 g of bis(triethylstannyl) acetylene in a sealed ampoule at 100 °C for 4 h. The resulting polymer was in the form of a white amorphous powder which decomposes without melting when heated above 180 °C. References 2 (Russian). [173-8831]

THERMAL STABILITY OF DI-IRON-HEXACARBONYL COMPLEXES OBTAINED FROM AROMATIC AZINES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 3, Mar 82 (manuscript received 12 Jun 81) pp 692-695

TRUSOV, V. V., NECHITAYLO, N. A., TYURIN, V. D., DZYUBINA, M. A. and
NAMETKIN, N. S., Institute of Petrochemical Synthesis imeni A. V. Topchiyev,
USSR Academy of Sciences, Moscow

[Abstract] A study was made of the thermal stability of di-iron-hexacarbonyl complexes obtained from aromatic azines. Study of the thermal decomposition of the compounds showed that their derivatograms are similar in nature. In all cases the DTA curves show a slight endothermic effect at the melting temperature of the complex, not accompanied by a decrease in weight. The derivatograms show that the iron carbonyl complexes decompose in three stages. The first is very rapid, featuring separation of three carbonyl groups. It is immediately followed by loss of three more CO groups. Above 210°C the products of decomposition of the ligands are liberated. Completion of the separation of these products occurs above 270°C. The temperature at which the decomposition of the complexes containing two 3-electron nitrogen-containing bridges begins is independent of ligand structure. References 9: 4 Russian, 5 Western.
[184-6508]

ACIDITY FUNCTION OF CONCENTRATED 12-TUNGSTOPHOSPHORIC ACID SOLUTIONS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3,
Mar 82 (manuscript received 19 May 81) pp 492-493

KULIKOV, S. M. and KOZHEVNIKOV, I. V., Institute of Catalysis, Siberian
Department, USSR Academy of Sciences, Novosibirsk

[Abstract] In order to estimate the catalytic effect of heteropolyacids in acid type reactions and to compare the strength of heteropolyacids with other mineral acids in concentrated solutions, the acidity function of one of the strongest heteropolyacids is measured in water, 40 vol.% aqueous dioxane and 94.5 vol.% HOAc with acid concentration not over 50% at 20°C. In all cases the acidity of the concentrated acid solutions is higher than for H₂SO₄ and HClO₄ by 1-1.5 H₀ units. References 9: 4 Russian, 5 Western.
[184-6508]

UDC: 541.6:541.49:547.567.2:546.811

SOME PROBLEMS OF STRUCTURE OF TIN-CONTAINING 3,6-DI-TERT-BUTYLORTHO-BENZOQUINONE COMPLEXES AND METALLOTROPIC CONVERSIONS IN THESE SYSTEMS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 19 Jun 81) pp 540-549

PROKOF'YEV, A. I., POMBRIK, S. I., KASYMBEKOVA, Z. K., BUBNOV, N. N., SOLODOVNIKOV, S. P., KRAVTSOV, D. N. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] A number of aromatic radicals with groups of various degrees of electronegativity were studied by EPR methods to clarify the details of radical metallotropy. Metal'otropy was found to result from two oppositely acting factors: the coordinating capacity of the central atom of the migrating fragment and the metal-oxygen bond strength. The EPR spectral parameters and spin density distribution in the free radical ligand of the tin-containing complexes studied depend on the nature of the substituent at the tin atom. The migration frequency in these radicals is determined by the strength of the SnO bond and the coordination saturation of the Sn atom as well as the spin density at the monovalent O atom. The polarity of the medium determines the direction of the ligand substitution reaction as orthoquinone interacts with monochlorine organic compounds of tin. In nonpolar media the organic ligand is substituted, in polar media such as DMSO the Cl atom is substituted. Figures 4; references 21: 12 Russian, 9 Western.
[184-6508]

UDC: 541.124:541.49:547.567.2:661.668

LIGAND SUBSTITUTION REACTION IN PARAMAGNETIC o-QUINONETETRACARBONYLMANGANESE AND TETRACARBONYLRHENIUM COMPLEXES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 9 Jul 81) pp 550-555

SARBASOV, K. , TUMANSKIY, B. L., SOLODOVNIKOV, S. P., BUBNOV, N. N., PROKOF'YEV, A. I. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] In order to determine the influence of the paramagnetic ligand on the mobility of CO groups, a study was made of the kinetics of ligand substitution in 3,6-di-tert-butyl-o-quinone(3,6-Q). To do this, a toluene solution of phosphite or amine of known concentration was added to a solution of 3,6-Q in toluene at about -70°C. The mobility of CO groups in orthoquinone complexes with tetracarbonylmanganese is significantly higher than in $Mn_2(CO)_{10}$. Figures 2; references 4: 2 Russian, 2 Western.
[184-6508]

ELECTROCHEMICAL STUDY OF OXYGEN ADDUCTS OF COBALT COMPLEXES WITH BENZALDEHYDE AROYLHYDRAZONES IN DIMETHYLFORMAMIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 5 Jun 81) pp 555-560

MUNIN, Ye. N., TROYEPOL'SKAYA, T. V. and KITAYEV, Yu. P., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, USSR Academy of Sciences

[Abstract] There is very little information available on oxygen-containing adducts of hydrazone complexes. The authors therefore studied the electrochemical behavior of CO complexes with benzoyl- and salicyloyl hydrazones of benzaldehyde in DMFA, finding certain anomalies in chemical behavior. The kinetic nature of the chelate reduction current in the second wave in constant-current polarography is explained by the splitting of attached oxygen in the process of electrolysis after transfer of the first electron. Cyclical volt-ampere measurement was used to record the formation of intermediate complex particles with the metal at 0 oxidation. Figures 4; references 8: 4 Russian, 4 Western.
[184-6508]

 α -HYDROXY- γ -[N,N-BIS(DIOXYPHOSPHORYLMETHYL)AMINO]PROPYLIDENEDIPHOSPHONIC ACID AS COMPLEXON

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 11 Aug 81) pp 560-564

SHCHERBAKOV, B. K., BEL'SKIY, F. I., KOMAROVA, M. P., POLIKARPOV, Yu. M., MEDVED', T. Ya. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] In order to study the complex-forming properties of the compound in the title, the authors studied its synthesis from the corresponding amino-substituted hydroxypropylidenediphosphonic acid by phosphonomethylation. The NMR spectrum of an aqueous solution of the compound contains two signals displaced relative to 85% H_3PO_4 by 8.4 and 17.3 md into the strong field area, indicating the presence of two nonequivalent P nuclei. The IR spectra of solutions in H_2O and D_2O were studied with pH (pD) corresponding to primary content of ionic forms of L^{8-} , HL^{7-} and H_2L^{6-} . The stability of complexes of the acid is increased by the presence of fragments of hydroxyalkylydenediphosphonic and iminodi(methylphosphonic) acids simultaneously in the molecule. Figure 1; references 18: 8 Russian, 10 Western.
[184-6508]

ORGANOPHOSPHORUS COMPOUNDS

UDC 541.63:547.1'118

STERICAL STRUCTURE OF 5-PHENYL-5-SELENO-1,3,5-DIOXA- AND 5-PHENYL-5-SELENO-1,3,5-DIAZAPHOSPHORINANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 1, Jan 82 (manuscript received 4 May 81) pp 127-131

ARBUZOV, B. A., YERASTOV, O. A., ZYABLIKOVA, T. A., IGNAT'YEVA, S. N., NIKONOV, G. N., ARSHINOVA, R. P. and KADYROV, R. A., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch, USSR Academy of Sciences

[Abstract] The three-dimensional structure of 5-phenyl-5-seleno-1,3,5-dioxa- and diazaphosphorinanes was determined. Substituted 5-phenyl-5-seleno-1,3,5-dioxaphosphorinanes were found to exist in the form of stereo isomers distinguished by orientation of substitution at the phosphorous and carbon atoms. The stereo isomer is thermodynamically stable in the case of 5-phenyl-seleno-2,4,6-trimethyl-1,3,5-dioxaphosphorinane in a chair conformation with an axial phenyl at the phosphorus atom. The diazaphosphorinanes are a mixture of conformers distinguished by phenyl orientation at the phosphorus atom. Figures 1; references 14: 11 Russian, 3 Western. [128-6521]

UDC 542.951.1:541.49:547.1'118

ACYLATION OF β -KETOILIDES OF PHOSPHORUS BY ACID CHLORANHYDRIDES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 1, Jan 82 (manuscript received 4 Jun 81) pp 192-194

NESMEYANOV, N. A., BERMAN, S. T., REBROVA, O. A. and REUTOV, O. A., Moscow State University imeni M. V. Lomonosov

[Abstract] Only acyloxyvinylphosphonic salts are formed when β -oxoalkylidenetriphenylphosphoranes react with chloranhydrides of p-nitrobenzoic, cinnamic and phenylacetic acids. All presently known reactions of

β -ketoilides of phosphorus with chloroanhydrides of acids lead to O-acylation products. References 7: 4 Russian, 3 Western.
[128-6521]

UDC 547.341+541.67

APICOPHILICITY OF EXTRACYCLIC GROUP, STRUCTURE AND STABILITY OF SPIROPHOSPHORANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 1 Apr 81) pp 239-250

RAGULIN, V. V., PETROV, A. A., ZAKHAROV, V. I. and RAZUMOVA, N. A. (deceased),
Leningrad Technological Institute imeni Lensovet [Leningrad Soviet of
Workers' Deputies]

[Abstract] Apicophilicity of the extracyclic group is one factor determining the ability of spirobicyclic phosphoranes to enter the permutation isomerization process, i.e., permutation isomerization of ligands around the central phosphorus atom. An evaluation is made of the influence of apicophilicity of the extracyclic group on the structure and stability of spirophosphoranes. Spiro-1,2-oxaphosphol-4-enes, formed as the result of 1,4-cyclic-addition of acrolein and crotonic and cinnamic aldehyde to dioxaphospholanes with a 3-coordinated phosphorus atom, served as the subjects of study. These subjects were selected because of their different extracyclic substituents, making it possible to anticipate varying permutation stability among spirophosphoranes. Dioxaphospholane-1,2-oxaphosphol-4-enes were produced in the form of colorless oily liquids or white crystals. Their structure was proven by IR and NMR ^1H , ^{13}C and ^{31}P spectra analysis. It is demonstrated that crotonic and cinnamic aldehyde and dioxaphospholanes of 3-coordinated phosphorus form a mixture of diastereomeric spirobicyclic phosphoranes and the thermodynamically preferred reaction product is a diastereomer with anti-orientation of substituents at the phosphorus and alpha-carbon of the oxaphospholene ring. NMR ^1H and ^{31}P spectra demonstrate considerable participation of phenyl- and dialkylamido extracyclic substituents in $p_{\pi}-d_{\pi}$ interaction with vacant 3d-orbitals of 5-coordinated phosphorus. Permutational and thermal metastability result when extracyclic alkoxy groups are added to a molecule of dioxaphospholane-1,2-oxaphosphole-4-ene. It is suggested that the spin-spin interaction constant for phosphorus with the alpha-carbon atom can be used as a test indication of a stereoisomeric structure. Figures 3; references 13: 6 Russian, 7 Western.
[173-8831]

1,3-ALKADIENEPHOSPHONATES. STEREOCHEMICAL STUDY OF BROMINATION AND DEHYDRO-BROMINATION OF DERIVATIVES OF 1,3-ALKADIENE-1-PHOSPHONIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 7 Apr 81) pp 250-263

VAFINA, G. S., KOMAROV, V. Ya., ZAKHAROV, V. I. and IONIN, B. I.,
Leningrad Technological Institute imeni Lensovet [Leningrad Soviet
of Workers' Deputies]

[Abstract] Stereochemical factors exert considerable influence on the direction of reactions for halogenation of derivatives of unsaturated phosphonic acids. As a continuation of a study of stereochemical aspects of the reactivity of unsaturated organophosphorus compounds, a study is presented of bromination and subsequent dehydrobromination of dichloranhydrides and ethers of 1,3-butadiene-, 1,3-pentadiene-, 2-methyl-1,3-butadiene- and 2,3-dimethyl-1,3-butadienephosphonic acids. It has been established that the original 1,3-dienephosphonates are characterized principally by s-trans-conformation in relation to the $=C^2-C^3=$ bond. Alkadienephosphonates are brominated in CCl_4 at room temperature and prolonged holding or heating is required to complete the reaction. All products were separated in the individual state by means of vacuum distillation. An analysis of the PMR spectra of bromination products demonstrated that in all cases simple addition of the bromine takes place at a $C^3=C^4$ multiple bond remote from the phosphorus. Bromination of dichloranhydrides and ethers of 1,3-alkadiene-1-phosphonic acids results in formation of 3,4-dibromo-1-alkene-1-phosphonates. Dehydrobromination with the presence of hydrogen at the No 3 position results in formation of 3-bromo-1,3-alkadiene-1-phosphonates. It has been proven that the 3-bromo-1,3-alkadiene-1-phosphonates formed exhibit principally s-trans-conformation in relation to the $=C^2-C^3=$ bond. Dehydrobromination is inhibited in Z-isomers by polar interaction of the hydrogen in the No 3 position and the phosphonic group. This indicates a dehydrobromination mechanism whereby the hydrogen atom in the No 3 position is attacked by the base. Figures 4; references 13: 12 Russian, 1 Western. [173-8831]

CHLORINATION OF TERTIARY ALLENIC OXIDES OF PHOSPHINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 12 Mar 81) pp 264-268

ANGELOV, Kh. M., KHRISTOV, Kh. Zh. and IONIN, B. I., Higher Pedagogical Institute, Shumen, People's Republic of Bulgaria; Leningrad Technological Institute imeni Lensovet [Leningrad Soviet of Workers' Deputies]

[Abstract] Chlorination of the oxide of dimethyl(3-methyl-1,2-butadienyl)-phosphine in carbon tetrachloride results in formation of the chloride of

4-chloro-2,2,5,5-tetramethyl-1,2-oxaphosphol-3-ene (I). However, chlorination of the oxide of diphenyl(3-methyl-1,2-butadienyl)phosphine in carbon tetrachloride does not result in formation of a cyclic product and the chlorine is added at the $C^2=C^3$ double bond. The physical properties of this substance differ considerably from those of I. Chlorination of oxides of diphenyl(1,2-butadienyl)- and diphenylallenylphosphine also results in products of addition at the $C^2=C^3$ double bond. These differences in chlorination of tertiary allenic oxides of phosphine prove the considerable spatial influence of substituents at the phosphorus on the geometry of the transient state. It is suggested that the bulky phenyl radicals prevent overlapping of p-orbitals of the phosphoryl oxygen with the p-orbital of the carbonium ion formed at the intermediate stage, promoting addition of the chloride anion at the C^3 atom. It has been demonstrated that cyclic phosphonium compounds or products of addition at the $C^2=C^3$ double bond are produced depending on the substituents at the phosphorus. Replacing a single phenyl radical in the oxide of diphenyl(3-methyl-1,2-butadienyl)phosphine with chlorine results in formation of a cyclic oxaphospholene. Figures 3; references 10: 9 Russian, 1 Western.
[173-8831]

UDC 547.341

INTERACTION OF DIETHYL ETHER OF 2-ETHOXYETHENYLPHOSPHONOUS ACID WITH SUBSTITUTED NITRYLIMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 13 Apr 81) pp 268-272

PLATONOV, A. Yu., TROSTYANSKAYA, I. G., KAZANKOVA, M. A. and
CHISTOKLETOV, V. N., Leningrad Technological Institute of the Pulp and Paper Industry; Moscow State University imeni M. V. Lomonosov

[Abstract] It has been demonstrated that diethyl-2-ethoxyethenylphosphonite reacts with substituted nitrylimines in the presence of triethylamine according to a $3 + 3 = 6$ arrangement with elimination of the ethoxy group at the No 2 position of the multiple bond and the end products of these reactions are derivatives of 4-ethoxy-4-oxo-1,4-dihydro-1,2,4-diazaphosphorine. These derivatives have formulas of $C_{17}H_{16}N_3O_4P$, $C_{19}H_{19}N_3O_3P$ and $C_{14}H_{16}N_3O_6P$. The reaction represents a 1,3-dipolar $3 + 3 = 6$ cyclic addition reaction. An analysis was made of possible ways of forming these derivatives from the results of a gas-liquid chromatographic determination in the reaction mass of volatile components such as ethyl chloride, ethyl alcohol and diethyl ether. Data are presented on the change in concentration of ethyl chloride and ethanol in the reaction of diethyl-2-ethoxyethenylphosphonite with C-p-nitrophenyl-N-phenylnitrylimine. The analysis made it possible to conclude that the stabilization of intermediate cyclic ylides takes place by means of the protonation of the anion center by triethylamine hydrochloride with the subsequent detachment of the ethanol and formation of derivatives of 4-oxo-1,4-dihydro-1,2,4-diazaphosphorine. The structure and composition of the products was confirmed by elemental analysis and IR, PMR and NMR ^{31}P spectroscopic data. Values of chemical shifts in NMR ^{31}P

spectra testify to quaternization of the phosphorus atom during cyclic addition. A mixture consisting of 0.0025 mole N¹- α -chloro-p-nitrobenzylidene-N²-phenylhydrazine, 0.0075 mole triethylamine and 0.0025 mole diethyl-2-ethoxyethenylphosphonite in 30 ml absolute benzene was stirred while gradually being heated to 70 °C for 6 h in an atmosphere of argon to the point of cessation of the accumulation of ethyl chloride and ethanol among the reaction products, as checked by gas chromatography data. After the reaction mass was cooled, small quantities of triethylamine hydrochloride were filtered off, the solvent was eliminated by distillation and the residue was crystallized by trituration with ether. Six tenths of a gram (67 percent) of 1-phenyl-3-p-nitrophenyl-4-ethoxy-4-oxo-1,4-dihydro-1,2,4-diazaphosphorine were produced. References 6 (Russian). [173-8831]

UDC 541.57 : 546.17 + 546.18

PRESERVATION OF P-N BOND IN REACTION OF GAMMA-KETOALKYLAMIDOPHOSPHITES WITH PROTON DONOR REACTANTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 28 Oct 80) pp 272-277

MUKHAMETOV, F. S., STEPASHKINA, L. V. (deceased), RIZPOLOZHENSKIY, N. I. and SHAGIDULLIN, R. R., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch, USSR Academy of Sciences

[Abstract] The results are given of a study of reactions of hydrogen sulfide and thiophenol with methyldiethylamido(α,α -dimethyl- γ -ketobutyl)-phosphite (Ia), propyldiethylamido(α,α -dimethyl- γ -ketobutyl)phosphite (Ib), heptyldiethylamido(α,α -dimethyl- γ -ketobutyl)phosphite (Ic), tetramethyldiamido(α,α -dimethyl- γ -ketobutyl)phosphite (Id) and tetraethyldiamido(α,α -dimethyl- γ -ketobutyl)phosphite (Ie). It was shown that when hydrogen sulfide reacts with amidophosphites Ia to Ic and when thiophenol reacts with amidophosphite Ia the same crystalline substance is produced, which has been identified as trans-2-diethylamino-2-oxo-3,5,5-trimethyl-1,2-oxaphospholan-3-ol. A phosphoryl group was contained in the structure of the end product, and not a thiophosphoryl, and thianisole was identified in the liquid part of the reaction mixture in the case of thiophenol. These data prove that the reaction takes place through an intermediate quasi-phosphonium product. End products with P=O and P=S groups are formed, which is associated with the performance of two parallel reactions: 1) via an intermediate quasi-phosphonium product and 2) via substitution of the amido group at the phosphorus atom by the nucleophilic part of the proton donor reactant. It has been demonstrated that in the reaction of gamma-ketoalkylamidophosphites with proton donor reactants, preservation of the P-N bond is possible only when the reaction takes place through an intermediate compound of the quasi-phosphonium type. It has also been demonstrated that the importance of the reaction of substitution of the amido group by the

nucleophilic part of the proton donor reactant increases with an increase in the size of the alkoxy radical at the phosphorus atom or with its replacement by an amido radical. NMR ^{31}P data have demonstrated that increasing the size of the alkoxy radical at the phosphorus atom retards development of the reaction via the intermediate quasi-phosphonium compound. Because of this, the reaction rate for substitution of the amido group by an SH group can become comparable to or even exceed the rate of the reaction via the quasi-phosphonium product. The reaction of amidophosphites Id and Ie with H_2S and thiophenol can take place chiefly as a reaction of nucleophilic substitution of the amido group by SH or SPh groups.

References 7 (Russian).

[173-8831]

UDC 547.341

REACTIONS OF UNSATURATED COMPOUNDS, PART 82: INTERACTION OF VINYLALLENE PHOSPHONATES WITH ALCOHOLS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 30 Jan 81) pp 277-283

DANGYAN, Yu. M., PANOSYAN, G. A., VOSKANYAN, M. G. and BADANYAN, Sh. O.,
Institute of Organic Chemistry, Armenian SSR Academy of Sciences

[Abstract] The results are given of a study of the addition of alcohols to vinylallene phosphonates. 0,0-dialkyl-1-vinyl-3-methyl-1,2-butadienyl phosphonates with self-heating easily enter into a nucleophilic addition reaction with alcohols in the presence of a catalytic quantity of the appropriate alcoholate, resulting in 1,4-addition products. The diene phosphonates separated by distillation without removal of the catalyst are stable transparent liquids. Their structure has been confirmed by IR and PMR spectroscopy. The dienes extracted for the most part represent trans-isomers. Monitoring the reaction by means of the gas-liquid chromatography and PMR spectroscopy methods demonstrated that both cis- and trans-isomers of these diene phosphonates form in the process of the reaction. With an increase in the amount of catalyst used and the duration of the process the ratio of isomers increases in the trans-isomer direction. These data demonstrate that the cis-isomer is converted into a trans-isomer in the course of the reaction. It is hypothesized that with the attack of the anion on 0,0-dialkyl-1-vinyl-3-methyl-1,2-butadienyl phosphonates, three carbanions form, of which the most reactive, E and Z, result in products of 1,4-addition. The second slower reaction of isomerization of the cis-isomer into a trans-isomer takes place concomitantly. The trans-isomer is thermodynamically more stable. The diene phosphonates produced are easily hydrolyzed with formation of a mixture of cis- and trans-isomers of α,β -unsaturated phosphoryl-containing ketones with a 1:3 ratio, respectively. Figures 3; references 6: 5 Russian, 1 Western.

[173-8831]

AMINO ETHERS OF THIOPHOSPHORIC ACID, PART 7: THION-THIOL ISOMERIZATION OF AMINO ETHERS OF TRITHIOPHOSPHORIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 22 Dec 80) pp 309-316

GUPALO, A. P., KOVAL'CHUK, Ye. P. and KHMIL'OVSKAYA, M. I., L'vov Wood Technology Institute

[Abstract] The results are given of a study of some mechanisms for thion-thiol isomerization of amino ethers of trithiophosphoric acid as a function of the number of methylene groups, the structure of alkyl radicals at the nitrogen and sulfur atoms and the temperature and nature of the solvent. The original amino ethers were produced by alkylation of the appropriate potassium salts of O-(dialkylaminoalkyl)trithiophosphoric acid by means of halogen alkyls. The isomerization rate was studied by means of thin-layer chromatography using a procedure developed for the quantitative determination of substances. The dependence of the rate of thion-thiol isomerization of beta-amino ethers on the concentration, temperature and nature of the solvent was studied by using O-(2-diethylaminoethyl)-S,S-diethyltrithiophosphate (I) as an example. Methyl alcohol was used as the solvent. It was found that the isomerization rate is reduced with a reduction in the concentration of compound I. It is hypothesized that isomerization of beta-amino ethers takes place as an intramolecular reversible reaction of the first order. The irreversible reaction of dimerization of the unstable immonium salt with the formation of a piperazine salt takes place concomitantly. This process occurs more rapidly the higher the concentration of the original amino ether and the higher the temperature. It was found that with an increase in temperature the isomerization reaction rate increases insignificantly and the activation energy for this process is relatively low. The isomerization reaction rate for beta-amino ethers is determined to a considerable extent by the nature of the solvent and increases with an increase in its dielectric constant. The isomerization reaction rate for beta-amino ethers of trithiophosphoric acid depends slightly on the structure of alkyl groups around sulfur atoms, but the structure of groups around the nitrogen atom exerts a considerable influence. It was demonstrated that transformation of O-(3-diethylaminopropyl)-S,S-dipropyltrithiophosphate is of an intermolecular nature and is described by a kinetic equation of the second order for irreversible processes. It was found that O-(4-dialkylaminobutyl)-S,S-dialkyltrithiophosphates are unstable and that O-dialkylaminoalkyl-S,S-dialkyltrithiophosphates can be stabilized by converting them to oxalates. These oxalates are solid crystalline substances which are soluble in water and low alcohols and are insoluble in ether. The original amino ethers can be extracted from them by the effect of potassium hydroxide. Figures 1; references 12: 1 Russian, 11 Western.
[173-8831]

STUDIES OF SERIES OF DERIVATIVES OF PHOSPHINIC AND PHOSPHINOUS ACID,
PART 105: PHOSPHORYLATED ENAMINES AND THEIR E, Z-ISOMERIZATION

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 8 Apr 81) pp 316-322

ALIKIN, A. Yu., LIORBER, B. G., SOKOLOV, M. P., RAZUMOV, A. I., ZYKOVA, T. V.
and SALAKHUTDINOV, R. A., Kazan' Chemical Technology Institute
imeni S. M. Kirov

[Abstract] Studies are continued on the synthesis and reactivity of phosphorylated enamines belonging to triad systems activated by a phosphoryl group. A series of 11 compounds of this type have been produced and the results are given here of a study of their E, Z-isomerization. The goal of this work is to make it possible to study the composition of isomeric mixtures and the means of E, Z-isomerization and to study the mechanism of reactions of phosphorylated enamines with electrophilic olefins. Enamines with a primary amino group were prepared by admitting ammonia to alcohol or acetonitrile solutions of phosphorylated aldehydes and ketones. It was established by NMR spectroscopy that phosphorylated enamine II with a formula of $C_9H_{20}NO_3P$ exists in the Z-form and products VII, VIII and XI, with formulas of $C_9H_{20}NO_3P$, $C_{12}H_{26}NO_3P$ and $C_{11}H_{24}NO_3P$, respectively, exist in E-form. The remaining compounds are secondary phosphorylated enamines of ketones and are found in the form of a mixture of E- and Z-isomers. The results are presented of studies of the PMR and NMR ^{31}P and NMR ^{13}C spectra of the enamines studied. It is concluded that the E, Z-isomerization of phosphorylated enamines of ketones apparently takes place via the tautomeric imine form, whose lifetime is so short that it cannot be observed directly in NMR spectra. The direction of E- and Z-transformations depends on the nature of the substituents in the enamine triad; they determine the ability to form intramolecular and intermolecular hydrogen bonds. Figures 2; references 11: 8 Russian, 3 Western.
[173-8831]

UDC 541.64 : 547.241

IR SPECTRA AND FEATURES OF CONJUGATION EFFECTS IN COMPLEXES OF OXIDES OF
DIARYLMETHYLPHOSPHINES WITH PHENOL IN CCl_4

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 21 Jan 81) pp 323-327

SHVETS, A. A., GONCHAROVA, L. V., ZAVIRYUKHINA, N. Ye., MOISEYEVA, O. A.,
TALANOVA, L. N. and OSIPOV, O. A., Rostov-na-Donu State University

[Abstract] A study is presented of the spectral characteristics of the hydrogen bond implemented in solutions of complexes of phenol with diarylmethylphosphine oxides. Hypotheses are advanced regarding aspects of transfer of the substituent's electron effects to the phosphoryl group. Previous

studies (1980, 1982) had demonstrated that the greatest degree of conjugation of the aromatic ring and phosphoryl group in H-complexes of phenol with monoaryl and triaryl oxides of phosphines is achieved in triaryl compounds in which the phosphoryl group lies outside the plane of the phenyl ring. The diarylmethylphosphine oxides required for the study were produced by two methods: 1) when identical aryl groups are at the phosphorus atom, the individual oxides of phosphine were obtained by the action of arylmagnesium bromide on the dichloroanhydride of methylphosphonic acid and 2) for producing oxides of phosphines with different aromatic groups a reaction was employed for alkali decomposition of iodides of methyltriaryl phosphonium. A study was made of frequencies of hydroxyl absorption of phenol complexes with substituted diarylmethylphosphine oxides. When H-complexes with diarylmethylphosphine oxides are formed, the frequency of hydroxyl absorption is reduced by 340 to 350 cm^{-1} into the low-frequency region in relation to the value of 3612 cm^{-1} in non-associated molecules of phenol. It is demonstrated that both the spectral and energy characteristics of the hydrogen bond depend on the electron nature of the substituent. It is hypothesized that the effects of conjugation in oxides of diarylmethylphosphines are not great and that the influence of the substituent on the reaction center is transmitted primarily through an induction mechanism. It is concluded that the degree of conjugation of the substituent with the phosphoryl group in complexes of diaryl oxides lies midway between that in complexes of monoaryl and triaryl oxides of phosphines. The degree of conjugation of the aromatic ring and phosphoryl group increases successively when going from mono- to di- and triaryl oxides of phosphines. The overall sensitivity of the phosphoryl group to the influence of the substituent diminishes successively in that order. References 9: 5 Russian, 4 Western. [173-8831]

UDC 547.455 : 546.183

3,5,6-BICYCLOPHOSPHITES OF 6-AMINO-6-DESOXY- AND 3-AMINO-3-DESOXY-1,2-O-ISOPROPYLIDENE- α -D-GLUCOFURANOSE

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(manuscript received 17 Dec 80) pp 418-426

RUMYANTSEVA, S. A., KOROTEYEV, M. P., LYSENKO, S. A., SHASHKOV, A. S. and NIFANT'YEV, E. Ye., Moscow State Pedagogical Institute imeni V. I. Lenin; Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] A description is given of the production of aminodesoxy sugars containing an amino group at the primary and secondary carbon atoms, i.e., derivatives of 6-amino-6-desoxy- and 3-amino-3-desoxy-1,2-O-isopropylidene glucofuranose. A discussion is then presented of phosphorylation of aminodesoxy sugars and of the properties of the bicyclic amidophosphites produced. Descriptions are given of synthesis for the first time of 3,5,6-bicyclopophosphites

based on 6-amino-6-desoxy- and 3-amino-3-desoxy-1,2-O-isopropylidene- α -D-glucofuranose. 6-Amino-6-desoxy-1,2-O-isopropylidene- α -D-glucofuranose (IV) was produced by adding 1.84 g of triphenylphosphine to a solution of 1.44 g of 6-azido-6-desoxy-1,2-O-isopropylidene- α -D-glucofuranose (VI) in 10 ml of absolute pyridine, and then holding the mixture at 20 °C for 2 24-h periods. Then 6 ml of 25-percent aqueous ammonia were added and after 5 h at 20 °C the solution was boiled down and subjected to column chromatography. The entire triphenylphosphine oxide and then compound IV were removed by elution with methanol. The 3,5,6-O,O,N-bicyclophosphite of 6-N-phenylamino-6-desoxy-1,2-O-isopropylidene- α -D-glucofuranose (XIII) was produced by desiccating by means of repeated distillation with absolute benzene a solution of 682 mg of 6-N-phenylamino-6-desoxy-1,2-isopropylidene- α -D-glucofuranose (II) in 10 ml of absolute benzene; then 0.98 ml of dry triethylamine was added to a solution of the substance in 15 ml of absolute benzene. The solution was cooled to 0 to 5 °C and with vigorous stirring 0.20 ml of phosphorus trichloride was added dropwise. The mixture was held at 30 to 50 °C for 1 h and the triethylamine hydrochloride (99 percent) was filtered off. The solution was then vacuum-distilled and the residue was chromatographed. The NMR ^{13}C method was employed to prove the structure of the amino sugars produced and of the products of their phosphorylation. References 16: 4 Russian, 12 Western. [173-8831]

UDC 547.1'118

SINGLE-ELECTRON TRANSFER IN REACTION OF S-ETHYLDIPHENYLTHIOPHOSPHINITE WITH 1-NITRO-1-PROPENE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 28 Jun 81) p 441

AL'FONSOV, V. A., GAREYEV, R. D.; GOL'DFARB, E. I., BATYYEVA, E. S., SHERMERCORN, I. M. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Branch, USSR Academy of Sciences; Kazan' Veterinary Institute imeni N. E. Bauman

[Abstract] It has been discovered that, in the reaction between S-ethyldiphenylthiophosphinite with 1-nitro-1-propene, only oxidation of the original phosphinite to S-ethyldiphenylthiophosphinate (I) takes place, instead of the simultaneous reactions in different directions usually observed in reactions of alkyl ethers of P^{III} acids with nitroolefins. This reaction takes place through the transfer of a single electron with the formation of an ion-radical pair which is then stabilized either through the recombination of partners or through disproportionation to form compound I. By the NMR ^{31}P method chemical polarization of ^{31}P nuclei was observed in the reaction process both in the original phosphinite and in the final phosphinate, whereby the resonance signal corresponding to the original phosphinite showed negative polarization and the signal for compound I was polarized positively. The composition and structure of compound I were established

by means of elemental analysis data and IR, NMR ^1H and ^{31}P spectra and compound I was produced by counter synthesis by oxidation of S-ethyldiphenylthiophosphinite with manganese dioxide. The constants and spectral data of both specimens agreed. The data obtained demonstrate that when the oxygen atom in the P-O-Alk fragment is replaced by sulfur the reaction direction with the attack of the phosphorus atom on the beta-carbon atom of the nitroolefin is inhibited with formation of the corresponding unsaturated derivative of phosphorus or phosphorane. References 2 (Russian). [173-8831]

UDC 546.18+547.26'118

REACTION OF ISOCYANATE PHOSPHITES WITH ALKYL AND ARYL ISOCYANATES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 7 Jul 81) pp 443-444

KOZHUSHKO, B. N., SILINA, Ye. B., POVOLOTSKIY, M. I. and SHOKOL, V. A.,
Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] It has been established for the first time that isocyanate phosphites react very easily with alkyl and aryl isocyanates to form a condensed heterocyclic system containing a 1,3,2 λ^5 ,4 λ^5 -diazadiphosphoethidine ring (I). Diazadiphosphoethidines I are colorless crystalline substances insoluble in ether and petroleum ether and slightly soluble in benzene and toluene, but soluble in chloroform and dioxane. They decompose when heated and do not dissolve in cold water. Compounds I are preserved without changes in the crystalline state in a closed vessel. Di- and triisocyanate phosphites react analogously with alkyl and aryl isocyanates. Compounds I are prepared as follows: To a solution of 0.03 mole diethylisocyanate phosphite in 30 ml anhydrous ether is added, at 20 °C while stirring, 0.03 mole alkyl or aryl isocyanate and the mixture is stirred for 20 to 70 h. The colorless residue is removed, washed with anhydrous ether and dried in a vacuum desiccator over P_2O_5 . Diazadiphosphoethidines with the following formulas have been produced: $\text{C}_{14}\text{H}_{26}\text{N}_4\text{O}_8\text{P}_2$, $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_8\text{P}_2$ and $\text{C}_{24}\text{H}_{30}\text{N}_4\text{O}_8\text{P}_2$. The structure of these compounds has been confirmed by measurement of molecular weights cryoscopically in benzene and by IR and NMR ^1H and ^{31}P spectra. Measurement results indicate diazodiphosphoethidines with a 5-coordinated phosphorus atom. References 1 (Russian). [173-8831]

REACTION OF SALTS OF HYPOPHOSPHOROUS ACID WITH EPICHLOROHYDRIN

Leningrad OBSHCHEY KHMII in Russian Vol 52, No 2, Feb 82
(manuscript received 28 Jul 81) pp 444-445

YUDELEVICH, V. I., FETTER, A. P., KOMAROV, Ye. V. and IONIN, B. I.,
All-Union Scientific Research Technological Institute of Antibiotics and
Enzymes for Medical Purposes

[Abstract] A study was made of the reaction between sodium and aniline salts of hypophosphorous acid and epichlorohydrin. The reaction takes place with a 3-fold excess of epichlorohydrin in aqueous ethanol with the formation of 2-oxo-4-oxy-1,2-oxaphospholane (I). There have hitherto been no descriptions of reactions of hypophosphites with halogen-containing small rings and the reaction studied here can be extended to other small rings. The phospholane produced is a transparent, colorless, hard-to-crystallize, undistillable oil which does not exhibit acid properties and reduces aqueous or alcohol solutions of silver nitrite, proving the existence of a P-H bond. References 2 (Russian).

[173-8831]

UDC 547.56+535.34; 542.91

REACTION OF N^1, N^2 -DIMETHYL- N^1 -CHLOROBENZAMIDINE WITH BUTYLDIFLUOROPHOSPHITE: N^1, N^2 -DIMETHYLBENZAMIDINIUMTETRAFLUOROPHOSPHORATE

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 52, No 2, Feb 82
(manuscript received 18 Aug 81) pp 445-446

MARKOVSKIY, L. N., SINITSYA, A. D., KAL'CHENKO, V. I., ATAMAS', L. I. and
NEGREBETSKIY, V. V., Institute of Organic Chemistry, Ukrainian SSR Academy
of Sciences

[Abstract] A study was made of the reaction of N^1, N^2 -dimethyl- N^1 -chlorobenzamidine with butyldifluorophosphite. This is an exothermic reaction forming short-lived N^1, N^2 -dimethyl- N^1 -difluorochlorobutoxyphosphoranylbenzamidine (I) which at -30°C rapidly and practically totally is isomerized into N^1, N^2 -dimethylbenzamidinumdifluorochlorobutoxyphosphate (II). Compound II is thermally unstable and after a few days at 20°C it almost totally disproportionates to form the more stable compound N^1, N^2 -dimethylbenzamidiniumtetrafluorophosphate (III) and an unidentified mixture of products. The disproportionation process is sped up at elevated temperatures. Compound III is obtained by adding slowly dropwise a solution of 0.022 mole butyldifluorophosphite in 15 ml chlorobenzene at -30°C to a solution of 0.02 mole N-chlorobenzamidine in 15 ml chlorobenzene. The reaction mixture is held for 1 h at -30°C and then for 20 h at room temperature, after which

the solvent is evaporated and the residue is vacuum distilled, after which the product is purified by low-temperature crystallization from a hexane + benzene mixture and by subsequent sublimation under vacuum. The yield is 30 percent in terms of N-chloroamidine and the product has a melting point of 105 to 108 °C with a chemical formula of $C_9H_{11}F_4N_2P$.

References 2 (Russian).
[173-8831]

UDC 547.341

REACTION OF TRIETHYL PHOSPHITE WITH FURFURAL OXIME

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 16 Jul 81) pp 448-449

OSIPOVA, M. P., KUZ'MINA, L. V. and KUKHTIN, V. A. (deceased), Chuvash State University imeni I. N. Ul'yanov

[Abstract] By heating triethyl phosphite with furfural oxime to 80 °C, O-substituted hydroxylaminophosphonates were produced. The reaction takes place at the oxime group and is accompanied by migration of a proton from the oxygen to nitrogen. O,O-diethyl- α -(O-ethylhydroxylaminofurylmethyl)-phosphonate was produced with a yield of 39 percent and a boiling point of 70 to 72 °C at 1.5 mm Hg. This compound has the formula $C_{11}H_{20}NO_5P$. When this reaction is carried out under more rigorous conditions, diethylphosphorous acid and the nitrile of furoic acid form.

[173-8831]

UDC 547.341

REACTION OF 2-BROMOETHYLENE COMPOUNDS OF TRIVALENT PHOSPHORUS WITH NITRYLIMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 14 Aug 81) pp 451-452

PLATONOV, A. Yu., MAYOROVA, Ye. D., AKIMOVA, G. S. and CHISTOKLETOV, V. N., Leningrad Technological Institute of the Pulp and Paper Industry

[Abstract] Diethyl-2-bromoalkenyl phosphonites were reacted with diphenyl-nitrylimine produced by thermal decomposition of 2,5-diphenyltetrazene, i.e., under conditions excluding protonation of intermediate ylides. Cyclic products were separated which turned out to be identical to the compounds synthesized from the same bromoalkenyl phosphonites and N^1 - α -chlorobenzylidene- N^2 -phenylhydrazine in the presence of triethylamine: 1,3,5-triphenyl-4-ethoxy-4-oxo-1,4-dihydro-1,2,4-diazaphosphorine (I) and 6-methyl-1,3,5-triphenyl-4-ethoxy-4-oxo-1,4-dihydro-1,2,4-diazaphosphorine (II). Ethyl

bromide was detected in the reaction mass in a quantity consistent with the yield of the principal product. Diphenylnitrylimine was added to bromo compounds of trivalent phosphorus by boiling in an atmosphere of argon the individual reactants for 1 h in absolute mesitylene, or for 4 h in absolute benzene. The production of a stable phosphonium salt in reactions of diphenyl(2-bromo-1-phenyl)ethynyl phosphine with diphenylnitrylimine generated at the moment of the reaction presents evidence in favor of elimination of the bromide anion by means of cyclic ylides of phosphorus with the formation of quasi-phosphonium salts. References 2 (Russian). [173-8831]

UDC 547.496.3 : 547.241

HALIDES OF BENZYLARYLPHOSPHONIUM AND THEIR COMPLEXES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 2, Feb 82
(manuscript received 31 Jul 81) pp 458-459

BAGROV, F. V. and VOLKOV, V. D., Chuvash State University imeni I. N. Ul'yanov

[Abstract] It has been demonstrated that complete amides of p-fluoro- and p-dimethyl aminophosphonic acid are easily alkylated in a benzene medium by benzyl bromide with electronegative substituents, i.e., Br and NO₂, in the p-position of the aromatic ring, whereby the following phosphonium salts are formed: tetraethyldiamino-p-bromobenzyl-p-dimethylaminophenylphosphonium bromide (I) and tetraethyldiamino-p-nitrobenzyl-p-fluorophenylphosphonium bromide (II). By boiling I in ethanol, [Me₂NC₆H₄(BrC₆H₄CH₂)P(NEt₂)₂]⁺Br⁻·C₂H₅OH (III) is produced and [Me₂NC₆H₄(BrC₆H₄CH₂)P(NEt₂)₂]⁺Br⁻·SnCl₂ (IV) is produced when I interacts with stannous chloride. The compounds separated were studied for structure and individuality by an element analysis for phosphorus and by means of IR and PMR spectra. IR spectra were recorded with an "IKS-14A" spectrometer in vaseline oil and PMR spectra with an "RYa-2308" spectrometer with an operating frequency of 60 MHz with CHCl₃ and HMDS as the internal standard. References 2 (Western). [173-8831]

UDC: 541.63:547.1'118

STERIC STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES, REPORT 26: SYNTHESIS AND STRUCTURE OF 2-DIALKYLAMINO-1,3,2-DIOXAPHOSPHEPANS WITH PLANAR GROUP OF ATOMS IN RING

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3,
Mar 82 (manuscript received 8 Jul 81) pp 588-593

ARBUZOV, B. A., KADYROV, R. A., KLOCHKOV, V. V., ARSHINOVA, R. P., and
AGANOV, A. V., Chemical Institute imeni A. M. Butlerov; Kazan' State
University imeni V. I. Ul'yanov-Lenin

[Abstract] The authors have begun a systematic study of the conformations of 1,3,2-dioxaphosphepans, the closest analogs to the more thoroughly studied

1,3,2-dioxaphosphorinanes, with a planar group of atoms in the ring. This report presents results of conformational analysis of 2-dialkylamino derivatives by NMR spectroscopy, the method of dipole moments and the Kerr effect. These studies of molecules with a benzene ring or double bond in the ring have shown the presence of conformation equilibrium between the chair form with equatorial position of dialkylamino groups and the twist form.
[184-6508]

UDC: 541.63:541.515:547.1'118

STERIC STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES, REPORT 28:
CONFORMATION OF PHENYL RADICAL IN 5-PHENYL-5-OXO(THIONO)-1,3,5-DIOXAPHOSPHORINANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 4 Jun 81) pp 594-599

KADYROV, R. A., ARSHINOVA, R. P. and ARBUZOV, B. A., Chemical Institute imeni A. M. Butlerov; Kazan' State University imeni V. I. Ul'yanov-Lenin

[Abstract] A study was made of the conformation characteristics of the phenyl-containing fragment of 5-phenyl-5-oxo(thiono)-1,3,5-dioxaphosphorinanes by means of the Kerr effect. The stereoisomers are convenient objects for study of the rotational isomery of the benzene ring around the P-Ph bond, since they exist in the form of two chair forms with a- and e- position of the phenyl. The Kerr constant was calculated considering the previously established structure of the ring. The Kerr constant was determined as a function of angle of rotation of the phenyl. The Kerr effect data indicated near parallel orientation of the benzene ring plane and the plane of the P=X (X=O,S) bonds. Optimal structural conditions are achieved for resonant interaction of the high orbitals of the phenyl radicals and the P=X bond. Figures 3; references 11: 10 Russian, 1 Western.
[184-6508]

STERIC STRUCTURE OF 5-PHENYL-5-OXO-2,4,6-TRIISOPROPYL-1,3,5-DIOXAPHOSPHORINANE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 25 Jun 81) pp 599-603

ARBUZOV, B. A., YERASTOV, O. A., LITVINOV, I. A., YUFIT, D. S. and STRUCHKOV, Yu. T., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, USSR Academy of Sciences; Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] The structure of an individual stereoisomer of the 5-phenyl-1,3,5-dioxaphosphorinanes (at the P) is studied by x-ray structural analysis. The stereoisomer mentioned in the title has a melting point of 215°C, chair conformation with equatorial orientation of all substituents. The conformation of isopropyl groups relative to the bonds of the ring is hindered. The benzene ring at the P atom is perpendicular to the plane of the heterocycle. Figure 1; references 14: 8 Russian, 6 Western. [184-6508]

ANISOTROPY OF POLARIZABILITY AND STERIC STRUCTURE OF TRIPHENYL- AND TRIMESITYLPHOSPHINES, THEIR OXIDES AND SULFIDES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3, Mar 82 (manuscript received 5 Jun 81) pp 604-607

TIMOSHEVA, A. P., ROMANOV, G. V., VUL'FSON, S. G., VERESHCHAGIN, A. N., STEPANOVA, T. Ya. and PUDOVNIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, USSR Academy of Sciences

[Abstract] The method of dipole moments, Kerr effect and depolarization Rayleigh scattering of light was used to study compounds of the type Y_3PX , where $X = NEP, O$ and S , $Y = Ph$ or Mes . The molecular ellipsoids of polarizability and conformations of triphenyl and trimesitylphosphine, their oxides and sulfides are presented. The high degree of symmetry of the molecules allows the angles of rotation of aryl radicals to be determined in the axial approximation. The angles of rotation of the aryl radicals around the C-P bonds are quite similar. References 20: 11 Russian, 9 Western. [184-6508]

INTERACTION OF DIOXYMETHYLPHENYLPHOSPHINE WITH ISOBUTYLESTER OF
DIPHENYLBORIC ACID IN PRESENCE OF NITRILES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3,
Mar 82 (manuscript received 25 Jun 81) pp 676-679

ARBUZOV, B. A., YERASTOV, O. A., NIKONOV, G. N., ZYABLIKOVA, T. A.,
YEFREMOV, Yu. Ya. and MUSIN, R. Z., Institute of Organic and Physical
Chemistry imeni A. Ye. Arbuzov, Kazan' Affiliate, USSR Academy of Sciences

[Abstract] The authors previously demonstrated that the reaction of dioxymethylphenylphosphine with isobutylester of diphenylboric acid probably occurs in two stages: the first forms diphenylboryloxymethyl-(oxymethyl)phenylphosphine, after which attachment of formaldehyde arising from the oxymethyl radicals into a P-C-O-B system occurs. The authors therefore study the conditions of separation of the stages and introduce new reagents to the second stage, capable of attaching to the P-C-O-B system. The reaction was studied by NMR spectroscopy. In the presence of nitriles the reaction does indeed occur in two stages, reesterification followed by attachment of nitriles to the P-C-O-B system of the reesterification product. References 7: 5 Russian, 2 Western.

[184-6508]

SYNTHESIS OF ETHYL-BIS(N-BUTYL-N-ISOBUTENYLAMIDO)PHOSPHITE AND INTERACTION
WITH α -CHLOROACETIC ALDEHYDES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3,
Mar 82 (manuscript received 2 Jul 81) pp 700-702

KIBARDIN, A. M., GRYAZNOV, P. I., GAZIZOV, T. Kh., IRAIDOVA, I. S. and
PUDOVIK, A. N., Institute of Organic and Physical Chemistry
imeni A. Ye. Arbuzov, Kazan' Affiliate, USSR Academy of Sciences

[Abstract] The ethylester of bis(N-butyl-N-isobutenylamido)phosphoric acid was synthesized by treating N-butyl-N-isobutenylamidodichlorophosphite with N-butylisobutyroimine and subsequent interaction of the bis(N-butyl-N-isobutenylamido)chlorophosphite formed with ethanol in the presence of triethylamine. Further interaction with mono- and dichloroacetic aldehydes and chloral produced bis(N-butyl-N-isobutenylamido)O-vinyl-(III), bis(N-butyl-N-isobutenylamido)O- β -chlorovinyl(IV) and bis(N-butyl-N-isobutenylamido)O- β , β -dichlorovinylphosphate(V). The insecticidal and herbicidal properties of these compounds were studied. The compounds had herbicidal activity, but not insecticidal activity. References 4: 3 Russian, 1 Western.

[184-6508]

SYNTHESIS AND STUDY OF COMPLEX FORMING PROPERTIES OF XYLYLENEDIAMINO-
TETRA(METHYLPHOSPHONIC) ACIDS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 3,
Mar 82 (manuscript received 11 Aug 81) pp 710-713

POLIKARPOV, Yu. M., BEL'SKIY, F. I., MATVEYEV, S. V., MEDVED', T. Ya. and
KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov,
USSR Academy of Sciences, Moscow

[Abstract] The m-(I) and p-(II) isomers of xylylenediaminotetra(methylphosphonic) acid were obtained by the usual method. In order to compare the complex forming properties, butyleneditetra(methylphosphonic) acid (III) was also prepared with a flexible alkylene bridge between the nitrogen atoms, whereas the bridges in acids I and II contain 5 and 6 C atoms in the same plane. The acid-base and complex forming properties of the compounds synthesized were studied potentiometrically in water. The position of the complex forming groups in the benzene ring was found to have no influence on the acid-base and complex forming properties of m- and p-isomers of xylylenediaminotetra(methylphosphonic) acid. References 8: 5 Russian, 3 Western.
[184-6508]

PESTICIDES

UDC 546.183

P^{III}-PHOSPHORYLATED HYDRAZONES OF ACETONE

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 2, Feb 82
(manuscript received 22 Jul 80) pp 196-200

GUSAR', N. I., RANDINA, L. V., PONOMARCHUK, M. P. and GOLOBOV, Yu. G.,
Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences

[Abstract] N-phenyl-N-(dialkoxyposphino)-hydrazones of acetone were produced by phosphorylation of phenylhydrazone of acetone with dialkylchlorophosphites and the reaction of P^{III}-phosphorylated hydrazones with phenylazide were investigated kinetically. High electron acceptor inductive capability of the Me₂C = NN(Ph) was shown. The interaction of methylchlorophosphite with phenylhydrazone of acetone in the presence of triethylamine also leads to 2-phenyl-5-methyl-1,2,3-diazaphosphol, produced as a result of splitting of the methyl alcohol molecule from the initially-formed 3-methoxy-2-phenyl-5-methyl-1,2,3-diazaphospholine-5. References 10: 7 Russian, 3 Western.
[147-6521]

UDC 547.78:422.435

INTERACTION OF BENZIMIDAZOLS AND AMINOXYRANES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 2, Feb 82
(manuscript received 5 Sep 80) pp 200-203

SOLOMKO, Z. F., AVRAMENKO, V. I., KHMEL', M. P. and MITYUKHINA, I. G.,
Dnepropetrovsk State University

[Abstract] The interaction of 2-alkyl(H)-benzimidazols and aminooxyranes-1-diethylamino-2,3-epoxypropane, 1-piperidyl-2,3-epoxypropane and 1-hexamethyleneamino-2,3-epoxypropane, produced by interaction of epichlorohydrin with the corresponding secondary amines and with subsequent treatment of the reaction mixture with caustic soda solution without separation of the

intermediate chlorohydrins, was studied. Derivatives of benzimidazol were produced by condensation of 1-dialkylamino-2,3-epoxypropanes with 2-alkyl-benzimidazols. The infrared and paramagnetic resonance spectra of the reaction products were given. References 10: 2 Russian, 2 Polish, 6 Western.
[147-6521]

UDC 620.197.3

PROTECTIVE PROPERTIES OF ENGINE OILS AND CORROSION INHIBITORS FOR THEM

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 3, Mar 82
pp 25-27

YERMOLOV, F. N., ENGLIN, A. B., VIGANT, G. T. and ZAKHAROVA, N. N.

[Abstract] The results are given of a study of the protective properties of USSR and foreign engine oils as compared with those of oils used strictly for storing engines and of combination oils which can be used both for operation and storage, as well as of the influence of corrosion inhibitors on them. These results indicate that the protective properties of individual engine oils are poor. Rust-preventive oil K-17 is good for protecting metals from the effect of an external corrosive medium but it has poor water displacement properties. The combination operating-and-rust-preventive oils Prot 20W/M and M-4z/8V₂G₁-RK have good protective properties and contain highly effective protective additives. Corrosion inhibiting additives AKOR-1 and KP display good protective properties when tested in sea water and a variable-temperature-and-humidity testing chamber, but they do not improve the water displacement properties of oils, even when added in large amounts. Corrosion inhibitor MSDA-1 cannot be used as an additive for combination operating-and-rust-preventive engine oils because of its corrosive effect on non-ferrous metals at temperatures of 60 and 70 °C and higher. MSDA-1 also loses its protective properties when heated. The polarization resistance method and the method of bringing different kinds of metals with different stationary potentials into contact with one another were employed to obtain data on the protective properties of combination operating-and-rust-preventive and inhibited engine oils. It is concluded that it is necessary to develop corrosion inhibitors which are more effective in terms of their protective properties than AKOR-1, KP and MSDA-1. In addition, corrosion inhibitors must be ash-free or have a low ash content and must be compatible with functional additives and must possess sufficient thermal stability and physical stability and not worsen the basic performance characteristics of engine oils, such as their cleansing, antioxidation, corrosion prevention and wear resistance properties. References 4 (Russian). [174-8831]

PHYSICOCHEMICAL PROPERTIES OF KARATYUBINSKOYE OIL AND JET ENGINE FUELS
PRODUCED FROM IT

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 82 pp 33-34

KHOKHLACHEVA, M. V., ZAKHARIDI, T. N., ZHMYKHOVA, N. M. and KRYLOVA, S. M.,
All-Union Scientific Research Institute of Oil Refining

[Abstract] The physicochemical properties of oil from the new Karatyubinskoye field in the Kazakh SSR are as follows: viscosity at 20 °C—19.06 mm²/s; pour point before heat treatment— -6 °C, and after heat treatment— -16 °C; sulfur content in percentage by weight—0.23; gold content—0.08; asphaltene content—1.80; silica gel resin content—7.80; paraffin content—2.98; paraffin melting point—54 °C; coking capacity—2.88 percent by weight; acid number—0.10 mg KOH/g; fractional yield—24.6 percent by weight for the 28-200 °C fraction, 21.9 for the 110-240 °C fraction and 52.1 for the up to 350 °C fraction. Jet fuels of various grades were produced by compounding close-cut fractions extracted in refining the oil in an ARN-2 unit. The 115-240 and 115-250 °C fractions fully satisfy the requirements of GOST [All-Union State Standard] 10227-62 for TS-1 fuel and of GOST 16564-71 for highly stable jet engine fuel. They have high thermal stability under static conditions, a low aromatic hydrocarbon and organic sulfur compound content, and a high heat value and luminometric number. The 50-250 °C fraction meets the requirements of GOST 10227-62 for T-2 fuel with a broad fractional composition. It surpasses the established norms for the content of aromatic hydrocarbons, heat value, thermal stability under static conditions, total and mercaptan sulfur content and height of the sootless flame. The 150-240 °C fraction meets the requirements of TU [Specification] 38-1-257-69 for T-8 hydrofined fuel. It has good density, sootless flame height, heat value and a low organic sulfur compound content, but is at the norm's margin in terms of thermal stability under static conditions. For producing T-8 fuel the appropriate straight-run fraction can be hydrofined for the purpose of improving its thermal stability. [174-8831]

UDC 66.022.37:678.763.43(047)

USE OF COPOLYMERS OF ETHYLENE AND VINYL ACETATE AS ADDITIVES FOR
PETROLEUM PRODUCTS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 3, Mar 82
pp 44-46

IVANOV, V. I., BASHKATOVA, S. T., ZAKHAROVA, E. L. and DINTSES, A. I.
(deceased), All-Union Scientific Research Institute of Oil Refining

[Abstract] A survey is presented of the applications of copolymers of ethylene and vinyl acetate as additives for petroleum products. Additives

such as ECA-5920, ECS-4242, ECA-5922 and Elwax are used both as depressor additives for diesel and heating fuels and as dewaxing additives for oils. Depressor additives improve the circulation of diesel, heating and boiler fuels. Copolymers with various molecular weights and a different content of vinyl acetate units in them are employed, depending on the specific area of application. Copolymers with a molecular weight of approximately 2000 and a 30-to-40-percent-by-weight vinyl acetate unit content exert the maximum depressor effect in diesel fuels, and a copolymer with an approximately 20-percent-by-weight vinyl acetate unit content can be used as a dewaxing additive for oils, but is not effective in diesel fuels. The addition of the additive VES-238 to summer diesel fuel makes it possible to lower its pour point to -35 to -60 °C depending on the brand of fuel. The addition of VES-238 to heating fuel in a quantity of 0.05 percent by weight makes it possible to produce winter grades of home heating fuel with a pour point of -30 °C and to lower the cold filterability point by 3 to 7 degrees. Copolymers of ethylene and vinyl acetate having a molecular weight of approximately 20,000 to 30,000 and a vinyl acetate unit content of approximately 24 to 34 percent by weight have been suggested as depressor additives for boiler fuels. The addition of 0.01 percent by weight of an ethylene - vinyl acetate copolymer additive to fuel oil results in lowering of the pour point by 13 degrees and by 40 degrees with a 0.1 percent by weight addition. These copolymer additives also reduce the dynamic viscosity of fuels and have been used successfully in dewaxing of oils and as additives which improve the viscosity index of petroleum oils. A molecular weight of about 5000 and a vinyl acetate unit content of 20 to 26 percent by weight are required for the last purpose. References 56: 46 Russian, 10 Western. [174-8831]

UDC 615.015.11 : 519.24

QUANTITATIVE RELATIONSHIPS BETWEEN STRUCTURE AND ACTIVITY IN CONSIDERING
INCONSTANT CONTRIBUTION OF SUBSTITUENT GROUPS TO BIOLOGICAL ACTIVITY OF
CHEMICAL COMPOUNDS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 3, Mar 82
(manuscript received 9 Oct 81) pp 325-330

ANTONOV, N. S., GEVENYAN, M. I. and TSEYROVA, L. T.

[Abstract] The authors cite data to the effect that the contribution, to a molecule's biological activity, of an identical replacing group at the same position may depend on the activity of the initial compound and the composition and site of other substituents groups in its molecule. They give examples of changes in toxicity of cardiac glucosides (a) by replacement of a formyl group by a hydroxymethyl group at position C₁₀ in genine and (b) toxicity of aglycones and products of their esterification by L-rhamnose at the C₃ hydroxy-group. These toxicity changes are tabulated. Experimental data are presented which suggest that every substituent brings its own change in the biological activity of the original molecule, and the magnitude and dimensions of those changes depend on some constant indicator of biological activity. Consequently, the change in activity should be predictable from knowledge of the nature of the substituent. Theoretical calculations are presented to exemplify this predictability. Figure 1; references 7: 1 Russian, 6 Western.
[180-12131]

SYNTHESIS AND BIOLOGICAL ACTIVITY OF ESTERS AND HYDRAZIDES OF PHOSPHORYLATED PHENYLACETIC ACIDS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 3, Mar 82
(manuscript received 6 Oct 81) pp 296-300

ISMAGILOV, R. K., RAZUMOV, A. I., ZHURAVLEVA, G. G., ZYKOVA, V. V.,
YAFAROVA, R. L. and BEZBORODOVA, T. A., Kazan' Chemical and Technological
Institute imeni S. M. Kirov; Mariyskiy University, Yoshkar-Ola

[Abstract] Continuing earlier related studies (KHIMIKO-FARMATSEVTICHESKIY ZHURNAL No 4, Apr 78 pp 79-83), the Arbuzov regrouping method was used to study the regrouping of ethyl esters of diethyl(and diphenyl)phosphonous acid under the action of ethyl esters of alpha-chloro(or bromo)phenylacetic acid. The structure of the products obtained was confirmed by nuclear magnetic resonance spectroscopy of ^{31}P , ^1H and ^{13}C . After their production, the products were tested for pharmacological value as sedatives for mice that had been subjected to electric shocks. Results indicated that the hydrazides of alpha-diethylphosphinylphenylacetic acid and of alphasdiphenylphosphinylphenylacetic acid did not have anti-cramping effects; the former had no effect on the orientation reaction or on muscular strength, while the latter suppressed both these functions. Details of the chemical procedures are presented in the chemical experimental section. Figure 1; references 6: 3 Russian, 3 Western.
[180-12131]

SYNTHESIS AND PHARMACOLOGICAL PROPERTIES OF 2-SUBSTITUTED 3-ARYL-3-HYDROXYQUINUCLIDINES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 16, No 3, Mar 82
(manuscript received 19 May 81) pp 307-311

BONDARENKO, V. A., TRUBITSYNA, T. K., ANISIMOVA, O. S., MIKHLINA, Ye. Ye.,
MASHKOVSKIY, M. D. and YAKHONTOV, L. N., All-Union Scientific Research
Chemical and Pharmaceutical Institute imeni S. Ordzhonikidze, Moscow

[Abstract] The title compound, which had not previously been described in the literature, was obtained by reacting 2-methylene-3-hydroxyquinuclidine with phenylmagnesium bromide. When the reaction mixture was treated with hydrochloric acid a hydrochloride of 2-hydroxymethyl-3,3-dioxyquinuclidine resulted. Hydrochlorides and methiodides of 2-methylene-3-aryl-3-hydroxyquinuclidines were studied for their effect on adrenal and choline systems and as antiarrhythmics, local anesthetics, cough suppressants and analgesics. None had adrenomimetic or antiarrhythmic effects. In toxic doses to mice

they caused breathing difficulties, slight tremors and cramps that increased with larger doses. One of the compounds, which was regarded to be a bicyclic analog of ephedrine, did not have the compound's stimulating effects. Thus the pharmacological value of these compounds was minimal. Details of the procedures used in synthesis are given in the experimental chemical section. References 11: 4 Russian, 7 Western.
[180-12131]

UDC 614.72:661.64]:613.155.3

REVIEW OF MAXIMUM PERMISSIBLE CONCENTRATION OF ARSENOUS OXIDE IN ATMOSPHERIC AIR OF POPULATED POINTS

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 82
(manuscript received 7 Apr 81) pp 6-9

KAMKIN, A. B., Sverdlovsk Scientific Research Institute of Labor Hygiene and Occupational Diseases

[Abstract] The toxic, embryotoxic and mutagenic effect of low concentrations of arsenic trioxide was studied during inhalation by rats. Chronic exposure of rats resulted in general toxic effects manifested in impaired function of the central nervous system, inhibited activities of a number of blood enzymes, accumulation of arsenic and histopathological changes in the parenchymatous organs. A concentration of 30 and of 3.0 micrograms per cubic meter also produced mutagenic and embryotoxic effects in the experimental animals. An arsenic trioxide concentration as low as 1.0 microgram per cubic meter had this embryotoxic action. A concentration of 0.3 microgram per cubic meter is recommended as the average annual maximum permissible level in the atmospheric air of populated points since it has no general toxic, mutagenic and embryotoxic effect. References 4: 3 Russian, 1 Western.
[131-6521]

UDC 614.73:615.31:546.79].033

ESTIMATING INHALATION ABSORPTION AND ACCUMULATION OF RADIOACTIVE SUBSTANCES IN NUCLEAR POWER PLANT REPAIR PERSONNEL

Moscow GIGIYENA I SANITARIYA in Russian No 1, Jan 82
(manuscript received 26 Mar 81) pp 29-31

VOROB'YEV, A. M., KOROTKOV, V. T., SIMAKOV, A. V., TSOV'YANOV, A. G. and STARODONOVA, N. P.

[Abstract] The inhalation absorption and accumulation of radioactive substances in repair personnel at nuclear power plants was determined and the

internal radiation dose was evaluated during work related to replacing the cutoff-control valves and spherical water flow regulators and repair of the main circulating pumps and separator drum at a nuclear power plant with an RBMK-1000 reactor. The inhalation absorption of β - and γ -radioactive substances comprises $2 \cdot 10^{-9}$ to $8 \cdot 10^{-9}$ curies per day and absorption of α -active substances comprises $1 \cdot 10^{-13}$ to $3 \cdot 10^{-13}$ curies per day. The absorption and accumulation were dozens and hundreds of times less than the maximum permissible dose. The annual accumulation of cesium-144 in the lungs comprises 16,000 picocuries, that of cobalt-60 comprises 8,000 picocuries, that of niobium-95 comprises 3,000 picocuries and the absorption of α -emitters comprises 2 picocuries in the lungs of repair personnel. The accumulation is approximately one order less in the skeletal bones, which is much less than the maximum permissible concentration. The calculated doses of internal radiation are equal to approximately 100 millirads per year to the lungs and 10 millirads per year to the skeletal bones, also dozens and hundreds of times less than the maximum permissible dose.

References 4: 1 Russian, 3 Western.

[131-6521]

UDC 677.494.743.21-96

PRODUCTION OF FLUORINE-CONTAINING F-50 THREADS BY EXTRUSION FROM MELT

Moscow KHIMICHESKIYE VOLOKNA in Russian No 1, Jan-Feb 82
(manuscript received 23 Jun 80) pp 13-14

KRONFEL'D, A. M., YEROKHOVA, V. A., LOGVINOV, A. I., LOGINOVA, N. N.,
BEZPROZVANNYKH, A. V., PANSIN, Yu. A. and VOL'F, L. A.

[Abstract] The fiber-flowing properties of F-50 fluoropolymer and formation of complex and monofilaments from it by extrusion of melt were investigated. The nature of flow of the F-50 melt and the main parameters of formation were established by differential thermal analysis. The filaments form at melting point of 340-360°C and at shear stress of not more than 450 kPa. Complex and monofilaments of F-50 are processed by traditional methods and can be used in the chemical industry, in the electrical engineering industry, in the shipbuilding industry, as an antifriction material and so on. The filaments are of specific interest to medicine due to their biological inertness. Figures 2; references 3 (Russian).
[148-6521]

UDC 677.022.78:677.017

EFFECT OF LASER HEAT TREATMENT ON STRUCTURE AND PROPERTIES OF CHEMICAL FILAMENTS

Moscow KHIMICHESKIYE VOLOKNA in Russian No 1, Jan-Feb 82
(manuscript received 8 Dec 80) pp 32-33

PUTNA, V. P., ZHIYEMYALIS, R. F. and PAKSHVER, A. B.

[Abstract] Changes in the structure of chemical filaments exposed to laser and to heat treatments during texturization were investigated by the false twisting method. Structural changes were determined by critical dissolution times, shrinkage during boiling, nonequilibrium, x-ray and infrared spectroscopy. Laser treatment differs from ordinary heat treatment by the fact that

during laser treatment the greatest structural changes occur on the surface layer rather than through the entire cross-section of the fiber. The strong surface effect of laser treatment may explain the high nonequilibrium of texturized filaments. References 5 (Russian).
[148-6521]

UDC 620.197:678.067.7

USE OF CARBON FIBERS IN CHEMICALLY STABLE APPARATUS

Moscow KHIMICHESKIYE VOLOKNA in Russian No 1, Jan-Feb 82
(manuscript received 23 Feb 81) pp 36-37

CHUKALOVSKIY, P. A., KONKIN, A. A., KUTSEBA, S. A., MELESHKO, A. I.
and FOMINA, N. I.

[Abstract] The effect of carbon fibers on the chemical stability of composite materials based on them is considered as a possibility of replacing stainless steels with structural polymer materials. A hybrid structural material was developed that combines the positive properties of glass-fiber-reinforced material with increased chemical stability of karboplast. The physical mechanical properties of the hybrid material are presented. The use of carbon fibers increases the operating life of articles based on them by a factor of 3-13 and results in an increase of the mean cycles between repair of equipment. A preliminary saving of 13,000 rubles is calculated due to the use of the hybrid composite material. The saving is increased to 35,000 rubles per ton of material if homogeneous leaded steel is replaced by the synthetic material. References 4 (Russian).
[148-6521]

UDC 678.043.6.678.01.539.3.4

SELENIUM SULFIDE OXIDE VULCANIZATION OF CHLOROPRENE RUBBER

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 81
pp 73-75

AKHMEDOV, G. G., BABAYEV, R. Kh., GASANOV, T. G., ATAKISHIYEV, N. K. and ABDYYEV, O. B., Institute of Chloroorganic Synthesis, AzSSR Academy of Sciences

[Abstract] Since vulcanates obtained by vulcanizing chloroprene rubber with bivalent metal oxides have relatively low levels of sub-vulcanization, and, sulfur oxide systems in the presence of Captax reduce thermal durability and vulcanization at 300% stretching, the authors studied the effects of selenium sulfides on physicomaterial properties of resins and blends based on chloroprene rubber. It was found that reducing sulfur content enabled

increased vulcanization at 300% stretching, while reducing residual stretch and shortening the time before sub-vulcanization began. In combination with Captax, selenium sulfide produced high performance rubbers while permitting relatively low vulcanizing temperatures. References 5: 4 Russian, 1 French (patent).

[186-12131]

UDC 678.046 : 539.612

STRUCTURAL CHANGES IN HIGH DENSITY POLYETHYLENE MODIFIED BY SILICON-CONTAINING MINERAL FILLERS

Baku AZERBAYDZHANSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 81
pp 76-82

ALIGULIYEV, R. M., Azerbaijan State Medical Institute imeni N. Narimanov

[Abstract] Polymer interaction with fillers can be characterized by physical adsorption, chemical reaction or both, depending on surface chemistry of the fillers, surface energy, the presence of lyophil particles and other factors. The authors studied fine-dispersion quartz, powdered silica gel, asbestos powder and kaolin in high density polyethylene crystalline structure to determine effects on crystallite dimensions, degree of crystallinity and elementary cellular parameters. For all fillers, an insignificant concentration level which brought increased effective dimensions was noted; for all but kaolin, a sharp decline was observed in this parameter after a certain level of concentration (15% for quartz fillers, 8-10% for others). With 15-20% filler material crystallinity fell below that of the original polymer. Thermodynamic factors were the chief determinant for crystallite dimensions at low filler concentrations. The latter two factors seemed related to declines in the segmental mobility of macromolecules in the hard surface. As the filler surface quantity grew, the quantity of the polymer in the layer where kinetic and spatial factors hampered crystallization increased and the general degree of crystallinity fell. Data of differential thermal analysis confirmed changes in thermal characteristics for the fillers tested. The best filler was judged to be quartz particles, although powdered silica gel gave similar spherulite fineness and homogeneity. Figures 4; references 14: 12 Russian, 2 English.

[186-12131]

UDC 678.762.3

ELASTOPLASTIC PROPERTIES OF SKI-3 AND SKI-3-01 RUBBERS

Moscow KAUCHUK I REZINA in Russian No 3, Mar 82
(manuscript received 22 Jun 81) pp 5-6

SIRE, Ye. M., AFANAS'YEV, S. V., KAMAYEVA, O. A. and POSPELOVA, L. M.,
Tol'yatti "Sintezkauchuk" Production Association

[Abstract] The modified resin SKI-3-01, in contrast to the original SKI-3 resin, contains diphenylamine groups attached to the polymer chains. Plasticity (P) and Mooney viscosity (M) are measured over a wide interval for samples of these two resins. The concentration of bound p-nitrosodiphenylamine in the SKI-3-01 is about 0.25%. P is related to M by the equation

$$M = a - b \cdot P$$

where a and b equal 133 and 158 respectively for SKI-3 or 165 and 222 respectively for SKI-3-01. The greatest difference in M is observed for P approximately equal to 0.30. The difference decreases for increasing P and disappears about P = 0.50, that is for lower molecular masses. Figure 1; references 6 (Russian).
[178-12027]

UDC 678.4:678.011:678.046

MODIFICATION OF SKI-3 RESIN WITH 2-HYDROXY-3-CHLOROPROPYLACRYLATE

Moscow KAUCHUK I REZINA in Russian No 3, Mar 82
(manuscript received 10 Jul 81) pp 6-7

BUTUSOVA, N. R., KOSTRYKINA, G. I., ZAKHAROV, N. D. and POLYAK, M. A.,
YaPI [Expansion unknown]

[Abstract] The addition of 2-hydroxy-3-chloropropylacrylate (OCPA) in the range 1.0 to 5.0 parts per 100 parts resin plus sulfur (2.5%), santokyr

(1.2%), zinc oxide (5.0%), and technical carbon black (trademark 75-50) to SKI-3 and natural rubber changes the relationship between % elongation and stress. The cohesive strength of the modified SKI-3 resins is higher than that for the unmodified resin and is close to that of natural rubber containing 3 wt % OCPA. Apparently this is due to the interaction between the SKI-3 and the carbon black which influences gel formation. Infrared spectroscopy was used to study the interaction between the resin and the carbon black. Other properties of the resin, such as resistance to tearing, strength under stress and hysteresis losses, improve somewhat with increasing cohesive strength. Figure 1; references 7: 6 Russian, 1 Western. [178-12027]

UDC 678.044.001.5:678.762.2-134.532

EFFECT OF RECEPTOR FACTORS ON REACTION EFFICIENCY OF ZINC DIALKYLDITHIOPHOSPHATE AS VULCANIZATION ACCELERATOR FOR SYNTHETIC BUTADIENE-NITRILE RUBBER

Moscow KAUCHUK I REZINA in Russian No 3, Mar 82
(manuscript received 25 Mar 81) pp 15-16

OVCHAROV, V. I., BLOKH, G. A., BLIZNYUK, T. G. and SAVENKO, A. I.,
Dnepropetrovsk Chemical Technological Institute imeni F. E. Dzerzhinskiy;
Belaya Tserkov' Technical Resin Products Plant

[Abstract] Data are reported on sulfur vulcanization of synthetic butadiene-nitrile rubber (SBR) for the two systems sulfur + accelerator and sulfur + accelerator + zinc dialkyldithiophosphate (Zn-DADTP). Accelerators considered include diphenylguanidine, Alta (a dibenzothioazole), thiuram, cimate, sulphenamide Ts and dithiodimorpholine. Except for the cimate + SBR system, the addition of Zn-DADTP to the reaction decreases the time to incipient vulcanization and increases the vulcanization rate. The magnitude of the accelerating affect is consistent with other accepted indications of chemical reactivity. The products obtained from the sulfur + accelerator + Zn-DADTP reaction show satisfactory physical-mechanical properties, are stable towards thermal aging and have strength and relative elongation values compatible to those of products obtained from the conventional single-accelerator systems. Figures 3; references 7 (Russian). [178-12027]

ADAPTIVE OPTIMAL DIGITAL CONTROL SYSTEM FOR POLYMERIZATION UNITS IN
PRODUCING DIVINYLS-STYRENE RUBBER

Kiev KHIMICHESKAYA TEKHOLOGIYA in Russian No 2, Mar-Apr 82 pp 31-33

AZHOGIN, V. V., ZGUROVSKIY, M. Z. and RUDENKO, S. S.

[Abstract] The emulsion polymerization process is crucial to high quality economical production of the title rubber; the authors have developed an algorithm for controlling this exothermal system that takes into account flow of cooling agents, mix of components and other production factors. The mathematical model was developed by first selecting a structure for the polymerization process system and identifying its parameters, and then optimizing the process functions using this model. The model was tested in the production of divinyl-styrene rubber, where it was used to determine that 80% of the costs of production were for raw materials and components of the aqueous phase of the process, and 19% were for degassing, coagulating and drying the rubber. The algorithm was judged to be simple and readily implemented on computers, and applicable to other multi-stage processes. Figures 2; references 3 (Russian).
[183-12131]

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